

PRINCIPLES OF HEAT
FOR DEGREE CLASSES

by

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LECTURER IN PHYSICS, UNIVERSITY OF DELHI

NEW
(THIRD)
EDITION

*Greatly Improved
and Enlarged*



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PREFACE TO THE THIRD EDITION

The book has been thoroughly revised. Many portions have been re-written. About 75 pages of new material and 50 new diagrams have been added and many old diagrams have been improved. An attempt has been made to make the book up-to-date. New topics like thermistors, thermostats, Zero-th law of thermodynamics, experimental verification of Maxwell's law of distribution of velocities, calorific value of food, regulation of body temperature, microcalorimetry, Nernst's calorimeter, law of conservation of energy, atomicity of gases, Partington's method for finding the ratio between the two specific heats of a gas, Hampson's method for liquid air, Maxwell's thermodynamic relations, determination of thermal conductivity by cylindrical tube method, Pirani gauge, production of high temperatures, electric furnaces, formation of clouds and artificial rain-making have been added. Laboratory methods for various determinations have been included. It is hoped that the book will now prove still more helpful to the students. Any suggestions for improvement will be thankfully received.

I am obliged to Shri Ram Lal Pury for correcting the proofs and for seeing the book through the press and for the great interest shown by him.

University of Delhi
1st December, 1954

HARNAM SINGH

PREFACE TO THE FIRST EDITION

Some apology is needed for placing a new-book on Heat in the market. The books already available to students do not meet their needs fully. Some contain too much of elementary stuff while others are too advanced. Moreover, students have to consult more than one book. An attempt has been made to present all that the students need in a very lucid form. Difficult portions like the Second Law of Thermodynamics, Reversible Processes, Radiation etc., have been treated very exhaustively. Numerical problems (mostly taken from university papers) have been solved and additional problems supplied for exercise. Questions are provided at the end of each chapter to enable the student to test his knowledge.

It is, however, for others to judge how far the author has succeeded in making the book useful. Suggestions for improvement will be thankfully received.

G. N. Khalsa College,
GUJRANWALA
October, 1945

HARNAM SINGH

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PRINCIPLES OF HEAT

CHAPTER I

THERMOMETRY

Experiment is the sole source of truth. But to observe is not enough . . . The scientist must set in order. Science is built up with facts as a house is with stones. But a collection of facts is no more a science than a heap of stones is a house—*Poincare*.

Historical. Heat and cold were recognized by Democritus as playing a vital part in the dynamic world of Nature, but he made no attempt to find how much heat and cold were present in any given situation. Galileo (1592) using an air-thermoscope was the first to give a method of roughly measuring temperatures independently of the sensation of touch, but he does not seem to have appreciated his discovery. To measure temperatures, a reproducible and accurate scale was necessary but no such standard was adopted during the 17th century. Thus Sagredo (1615) divided the interval between the greatest heat of summer and the extreme cold of winter into 360 parts. In 1632, Rey used a flask with a very narrow and long neck and holding water upto the neck. Rise of temperature was indicated by a rise in the water-level in the neck. This was the first liquid thermometer. In 1654 the tube was sealed off at the top and the effect of changing atmospheric pressure was eliminated.

In 1665 Boyle and Hooke suggested one fixed point—the melting point of ice—as the starting point. Shortly afterwards Fabri and Newton suggested two fixed points, 'the interval between the two to be divided in some manner to be agreed upon'. This suggestion was embodied in the Centigrade, Fahrenheit and the Reaumer scales which were developed during the 18th century. Both Fahrenheit and Reaumer were influenced by the earlier work (1701) of Amontons, to whom is also due the idea of an absolute scale of temperature. He was working with a gas thermometer and suggested that by extrapolation downwards below the lower fixed point one would reach a temperature, where "air would exert no pressure and will have no elasticity because its parts would be contiguous and cease to move." He suggested that this might be called the Absolute Zero of Heat-Content. Though his contemporaries merely laughed at this suggestion, it was amply confirmed by the work of Kelvin and Claussius during the 19th century.

1.1. Heat and Temperature. If a finger be dipped at short intervals in a cup of water placed over a lighted burner, the water feels warmer and warmer to the touch till it becomes too hot for the finger. We say that heat is passing from the burner into the cup and is changing the physical condition of the water contained in it and is making the water feel hotter and hotter to the touch.

Heat then is something which produces in us the sensation of warmth, while the degree of hotness of a body measured according to some agreed scale is called its **temperature**. *Heat then is the cause of a change of temperature.*

The direction of flow of heat, when two unequally heated bodies are placed in contact, is determined not by the amount of heat present in either body but by the difference in their temperatures. Heat always flows from a body at a higher temperature to the body at the lower temperature irrespective of the amount of heat present in either body, just as liquids always flow from a higher to a lower level irrespective of the amount of liquid present at either level. In this respect *temperature can be called level of heat*, and heat may be defined as energy which flows in response to a temperature-difference.

1.2. Mercury Thermometer. In a systematic study of the properties of Heat, an accurate measurement of temperatures is of the utmost importance and is generally the first thing that attracts the attention of the experimenter. An instrument for measuring temperatures is called a *thermometer*.

Properties of matter that *vary continuously with heating* are selected for measuring temperatures, taking care that the physical property selected has *not* the same value at two or more different temperatures and remains constant if the temperature does not change. The variation of the physical property which is used as the temperature-measurer should be sufficiently large to enable small temperature-changes to be indicated and measured. Expansion, change of resistance, change of vapour pressure, thermo-electric effect *etc.*, have been used for measurements of temperature. The various thermometers that are in use differ in the thermo-metric substance employed, the thermometric property utilized or in the function selected to represent the relation between the property and the temperature. The ideal thermometric scale would be one which made use of a property so selected that the scale would not depend on the thermometric substance. Such a scale would serve throughout the entire temperature-range, since no limitations due to failure or break-down of any substance would be made. The mercury-in-glass thermometer which uses the increase in the volume of mercury with heating, is the handiest instrument for such purposes and is a good temperature-measurer, unless *extreme* accuracy is the aim. Glass is selected as the envelop because it is transparent and easily reveals the level of the contained liquid, while mercury is selected because it is opaque, does not wet glass, has a low thermal capacity and its expansion in glass is fairly uniform.

Galileo constructed the first thermometer, though it was Amon-ton who first used mercury.

The thermometer consists essentially of a long glass stem having a uniform capillary bore and with a thin cylindrical bulb fused to it at one end. The bulb is kept thin so that heat may flow quickly into or out of the mercury inside it. The bulb and the stem are filled with pure mercury and heated to a temperature a few degrees above the highest temperature that is desired to be measured with that thermometer.

Some of the contained mercury expands and overflows. The top of the stem is then hermetically sealed off. Two fixed points—one near the top of the stem, called the **upper fixed point**, and the other near the bottom called the **lower fixed point**—are marked on the stem. The upper fixed point corresponds to the temperature at which pure water boils under a pressure of one atmosphere while the lower fixed point corresponds to the melting point of pure ice. These two fixed points have the convenience that they can be easily reproduced. The interval between the fixed points is divided into a number of equal parts called *degrees*. There are 100 degrees on the Centigrade scale, the lower point being 0 and the upper 100, while there are 180 degrees on the Fahrenheit scale, the lower point being 32 and the upper 212. Zero on Fahrenheit Scale indicates the lowest temperature then attainable by mixing salt and ice.

To convert from one scale of temperature to the other, we use the relation.

$$\frac{C}{100} = \frac{F - 32}{180}$$

where C is the temperature on the centigrade scale and F the corresponding temperature on the Fahrenheit scale.

1.3. To get an accurate value of temperature, various corrections have to be applied to the readings of a mercury thermometer. The more important sources of error are :

(1) *Due to the non-uniformity of the bore* of the capillary. It can be corrected by introducing a short length of mercury into the capillary. The thread of mercury is moved into various positions all along the tube and its length measured in each case. If these lengths are different, the bore is not uniform. From the measured lengths a correction can be found for all points of the capillary.

(2) *Due to the exposed stem*—the mercury in the stem is always at a temperature different from that in the bulb. Let the reading of the thermometer when n° of thread are exposed be t° and let the average temperature of the exposed part be θ and let α be the apparent expansion of mercury in glass. If the n° were warmed from θ to t , they would expand by $n \cdot \alpha \cdot (t - \theta)$ and therefore the corrected temperature is $t + n\alpha(t - \theta)$

(3) *Shift of the zero point of the thermometer*—when heated the bulb softens and the weight of mercury elongates the bulb and the zero point moves down. This has been reduced by the use of a special glass.

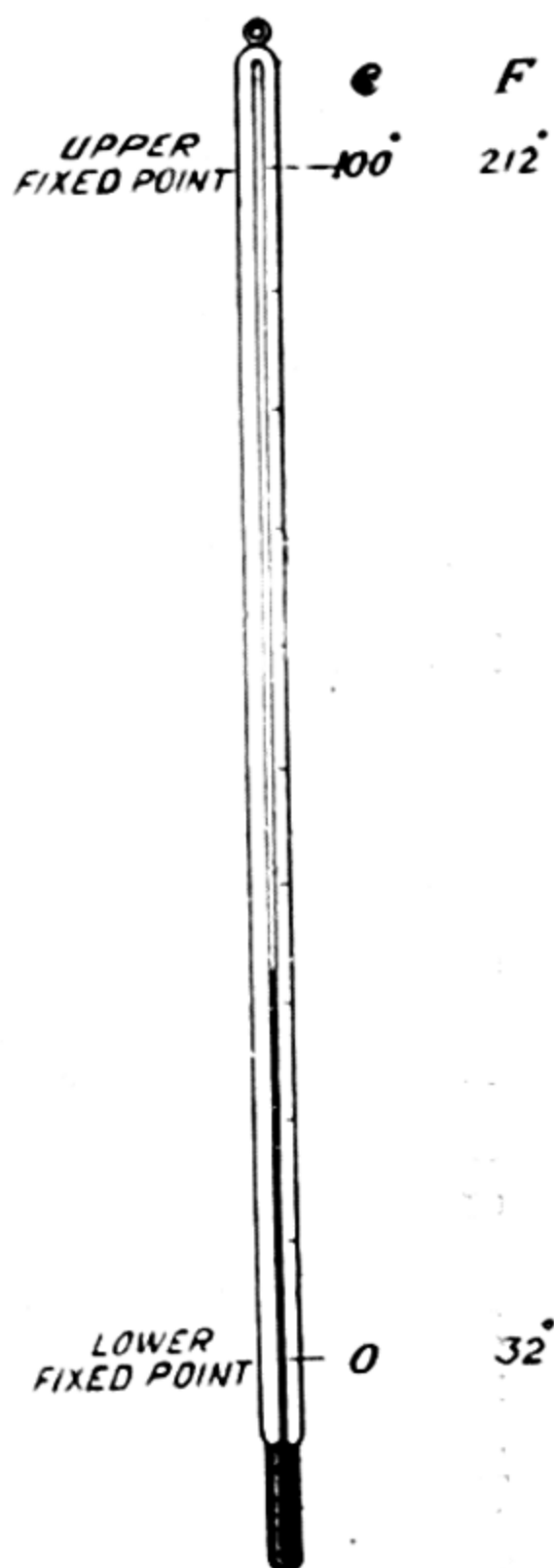


Fig. 1.1.
Mercury Thermometer.

1.4. Merits and Demerits of a Mercury Thermometer. The mercury thermometer possesses the following advantages :—

- (1) *It is small in size and is therefore portable.*
- (2) *It is very easy to use.*
- (3) *It is direct-reading.* The position of the meniscus of mercury gives the temperature directly.

The mercury thermometer is, however, not capable of great accuracy, because :

(1) *The expansion of glass is irregular* and as the co-efficient of expansion of mercury is not very different from that of glass, an error is introduced in the result, because graduations are made on the stem on the assumption that mercury expands uniformly in the glass, when heated.

(2) The expansion of mercury in glass is very small hence the instrument cannot detect small changes of temperature.

(3) When heated to a high temperature, the glass bulb softens and the weight of the mercury in it tends to elongate it. This produces a shift of zero and makes all graduations incorrect.

(4) *No two properly constructed mercury thermometers will ever agree in their readings* because the properties of glass are changed in the act of blowing the bulbs and therefore no two bulbs will expand or contract alike.

(5) *The mercury thermometer has a very limited range*,— 30°C to 250°C : hence it can only be used for measuring temperatures that are neither too low nor too high. To read higher temperatures a gas, usually hydrogen or nitrogen, is filled above the mercury in the stem. This elevates the boiling point of the liquid and thus prevents the distilling of the liquid to the upper parts of the stem which are cooler. Using a quartz bulb the scale can be extended upto 600°C but a new graduation will have to be put on the thermometer because the density of the contained gas will change as the temperature rises.

1.5. In order to obtain accurate results with a mercury thermometer it is necessary.

(1) That a sufficient length of it must be immersed in the bath whose temperature it is to measure.

(2) To allow it sufficient time to take up the temperature of the bath.

(3) To prevent a shift of zero which is liable to be produced when the bulb is over-heated or over-cooled.

(4) That the capillary tube *i.e.*, the stem must have a uniform bore.

(5) That the thermometer must be used in the same position in which it was calibrated, *e.g.*, if it was calibrated in the vertical position it must always be held vertically while reading temperatures.

1.6. Open-air Temperature. The measurement of open-air temperatures is influenced by the colour and surface of the thermometer. A freely suspended thermometer attains equilibrium with its

entire surroundings including the radiation which is always changing. It is necessary that the thermometer meant for measuring open-air temperatures be shielded because *the temperature of air is proportional to the kinetic energy of its molecules only* and therefore any radiations must be prevented from falling on the bulb of the thermometer.

1.7. Beckmann Thermometer. It is an accurate form of a mercury thermometer used for measuring small changes of temperature with considerable accuracy. It finds an application in the study of the influence of dissolved substances on the freezing and boiling points of liquids. The stem is marked from 0° to 5°C . and each degree is further sub-divided into 100 equal parts. In order to avoid errors due to irregular motion of mercury in a very fine tube, a tube of comparatively larger bore is employed, but the walls of the bulb are made very thin so that the instrument may be capable of furnishing quick changes of temperature.

A reservoir R is provided at the top of the instrument; this enables its range to be varied. For this purpose the bulb is heated, when some of the mercury expands into the reservoir and can be separated from the main column by gently tapping it. It is then placed in a bath along with another mercury thermometer and the temperature of the bath is gradually altered so that the reading on the former is zero; temperature on the other mercury thermometer is also read—this temperature corresponds to the zero on the Beckmann thermometer. The amount of mercury in its bulb is again altered as before, till its zero reading is close to the desired range.

To measure temperatures below zero, mercury is added to the stem. For this purpose the bulb is warmed so that the mercury expands just upto the entrance to the reservoir. The thermometer is then inverted to connect the mercury in the reservoir with that in the stem and when the bulb is allowed to cool, some extra mercury is drawn into the stem. Any excess can be disconnected in the usual way by gentle tapping when the thermometer is placed in the up-right position.

Thus if the mercury is at the top of the stem (*i.e.* at 5°C) when a subsidiary thermometer reads zero, temperature will be -5°C when the mercury in the Beckmann thermometer stand at zero. If more mercury is now added to fill the stem so that the mercury is again filling the stem upto the top, a further range of -5° to -10°C . can be obtained.

The accuracy of this instrument, however, changes with the amount of mercury present in its bulb. As the amount of the latter is changed to obtain various ranges of temperature, corrections must be applied to its readings. For this purpose correction curves are supplied with these instruments. Another correction has to be

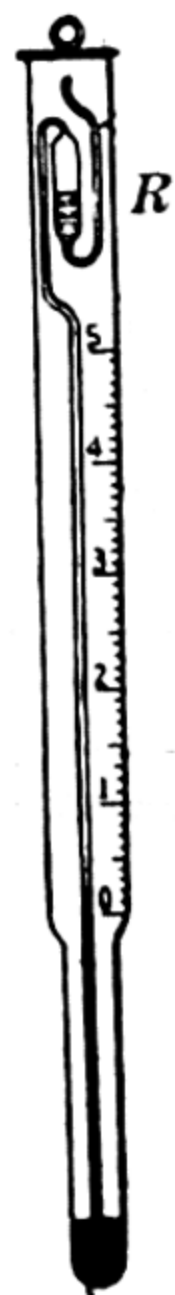


Fig. 1.2.
Beckmann
Thermometer.

applied for the emergent column, *i.e.*, for the fact that the mercury in the stem is not as hot as that in the bulb.

1.8. Maximum and Minimum Thermometers. It is sometimes desired to know the highest or the lowest temperature reached during a certain interval. Special thermometers are used for these purposes.

In the *maximum* thermometer the expansive force of the mercury forces it across a constriction in the stem during a rise of temperature. When, however, the temperature falls the column breaks at the constriction because the weight of the mercury above it is too insignificant to force the mercury down. In another type (Fig. *iii*), when the

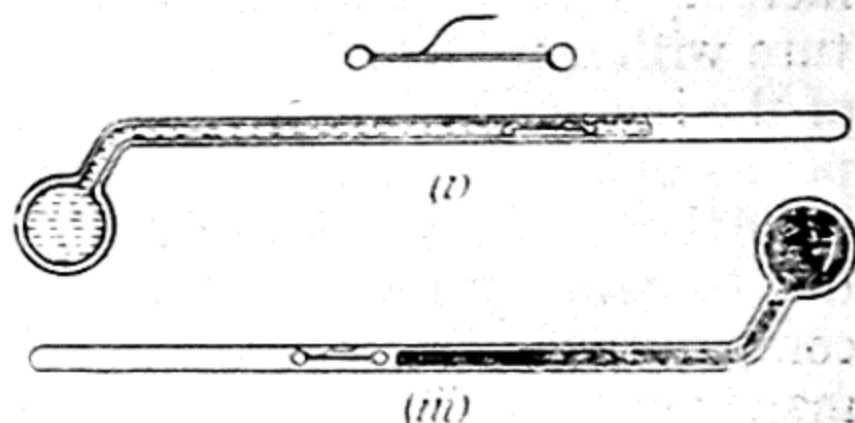


Fig. 1.3.

Max. and Min. Thermometer.

the mercury expands it pushes the steel index forwards, but when during a fall of temperature the meniscus recedes, it *leaves* the index behind. The *minimum* thermometer (Fig. *ii*) uses alcohol. During a rise of temperature the alcohol expands past a steel index lying in the stem. When, however, the temperature falls, on account of the concave shape of its meniscus, the surface tension of the contracting alcohol drags the index backwards. In either case the end of the index *nearest* the meniscus gives the required maximum or minimum temperature.

1.9. Gas Thermometers. A gas thermometer is preferable to a mercury thermometer as the expansion of gases is much larger and more uniform. The constant-pressure type instrument is not very accurate, because the gas which expands into the graduated tube on heating the bulb is not as hot as the gas in the bulb. To avoid this, Callender devised a *compensated air thermometer*. The thermometer tube *T* is connected directly with the graduated mercury

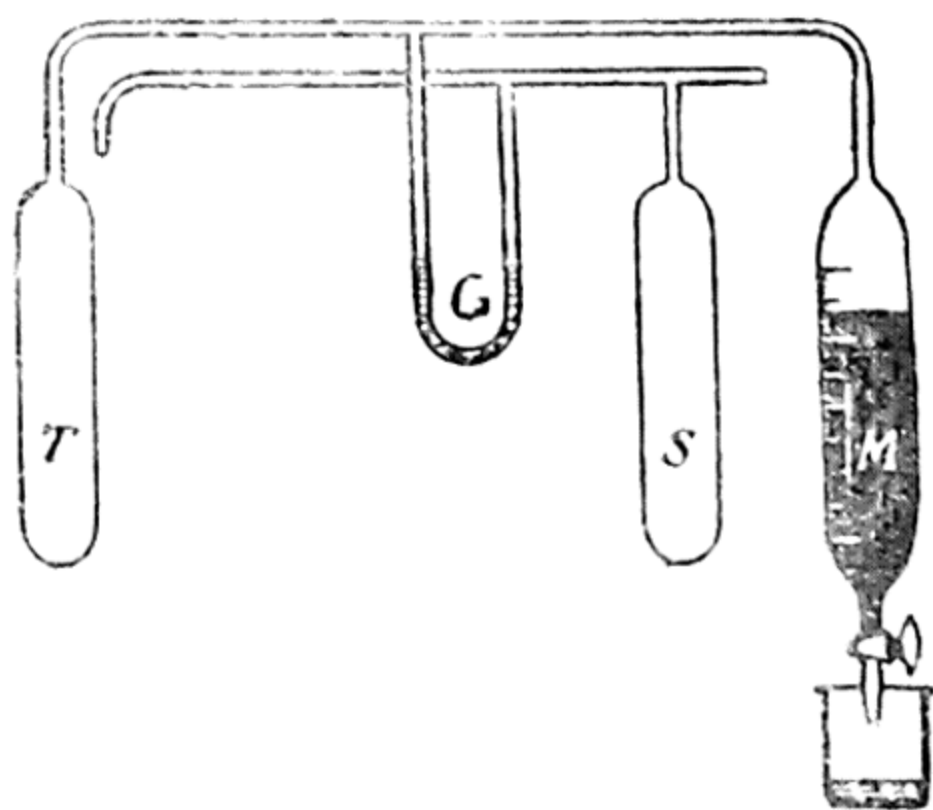


Fig. 1.4.

Callender's Air Thermometer.

tube *M* and indirectly through a sulphuric acid pressure gauge *G* with the bulb *S* which is filled with dry air and is constantly surrounded with melting ice. The pressure in *S* is therefore constant and independent of the atmospheric pressure. *T* is placed in melting ice and the level of mercury in *M* is adjusted till the gauge shows that the pressures in *S* and *T* are equal. To determine the temperature θ of a bath, *T* is placed in it and the level of mercury in *M* (which is also surrounded with

ice) is adjusted so that T and S are again at the same pressure. Then

$$\theta = \theta_0 \frac{T}{S - M}$$

where θ is the absolute temperature of the bath, θ_0 that of ice ($=273^\circ A$) and T , S , and M are the volumes of air in these tubes respectively. In this apparatus, errors due to the unknown temperature of air in the tube connecting T and M is eliminated by placing beside it a tube of the same size but joined to S .

Callender claimed a very high accuracy for his thermometer because (i) the apparatus and the calculations are simpler (ii) the pressure of the gas in T does not rise when the tube is heated.

The instrument, however, does not give consistent results at high temperatures. Hence in actual practice constant-volume type gas thermometers are always used.

1.10. Joly's Air Thermometer. It consists of a glass globe A continued in a capillary tube bent twice at right angles. The lower end of the capillary is connected to a tube R , full of mercury, by means of a rubber tube. The apparatus is suitably mounted on a stand. A is filled with dry air. It is then surrounded with pure melting ice. The air in A contracts. The level of mercury in X is adjusted by changing the position of R on the vertical stand so that the mercury stands upto a mark X in the capillary and the difference h , in the level of mercury in the two limbs is noted. Adding it to the barometric height we get the pressure P_0 exerted by the air at $0^\circ C$. (If the mercury in R stands lower than in X , the height h must be subtracted from the barometric pressure.)

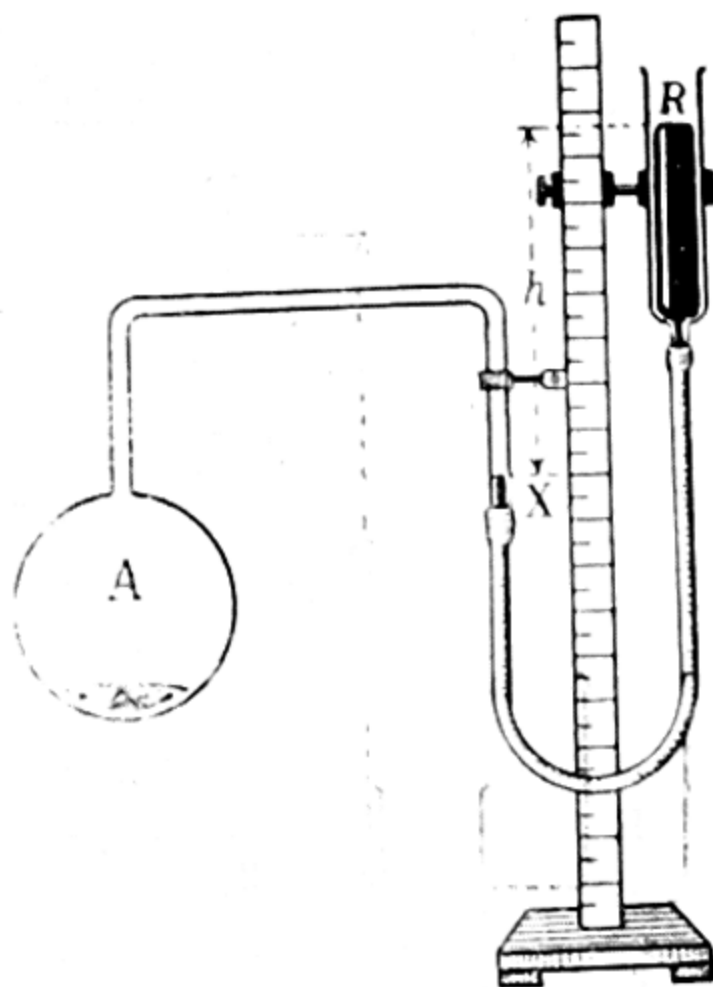


Fig. 1.5.
Joly's air Thermometer.

A is next surrounded by steam at $t^\circ C$ and the height of R is again adjusted till the mercury stands exactly at X in the capillary and the difference of heights h_t , noted, whence the pressure, P_t , of the enclosed air at t° is determined.

Next, the bulb A is surrounded by the bath whose temperature, x , it is desired to measure. The height h_x is similarly determined and the pressure P_x at x° found.

Now

$$P_t = P_0(1 + \gamma t)$$

or

$$\gamma = \frac{P_t - P_0}{P_0 \cdot t}$$

... (i)

Also

$$P_x = P_0(1 + \gamma x)$$

or

$$x = \frac{P_x - P_0}{P_0 \cdot \gamma}$$

Substituting the value of γ from (i),

$$x = \frac{P_x - P_0}{P_t - P_0} \cdot t.$$

It will be observed that the air in A has throughout the same volume *i.e.*, upto X , *i.e.*, it is being heated at constant volume. As the volume of air in the capillary is very small as compared with the volume of air in A , the error due to the fact that this air is not at the same temperature as that in A , is negligible. An error is introduced due to the fact that the volume of the bulb changes when it is heated or cooled, but a correction can be applied for this by filling it one-seventh with mercury. The expansion of mercury is then equal to that of the bulb A at all temperatures and the volume occupied by air in A remains constant throughout. The instrument has the following defects :—

To calculate the pressure exerted by the air in A the difference of levels of the mercury in the two limbs has to be added to or subtracted from the atmospheric pressure, but.

(i) the barometer may be at a vertical height different from the gas thermometer and will not therefore give the pressure at the level of the thermometer.

(ii) the atmospheric pressure might change appreciably while readings on the gas thermometer are being taken.

Hence, this gas thermometer cannot claim a high accuracy.

In a better form of a gas thermometer, a barometer is incorporated in the thermometer itself.

1.11. C. V. Hydrogen Thermometer. It consists essentially of a cylindrical bulb T of about a litre capacity made of an alloy of Platinum and Rhodium (which can withstand high temperatures) filled with hydrogen¹. At high temperatures hydrogen begins to flow across the walls of the bulb. It is therefore replaced by nitrogen, when high temperature measurements are to be made. T is joined to a glass tube T_1 with a narrow capillary tube and by adjusting the level of the mercury reservoir R , the mercury in T_1 is always made to touch the ivory tip P_1 .

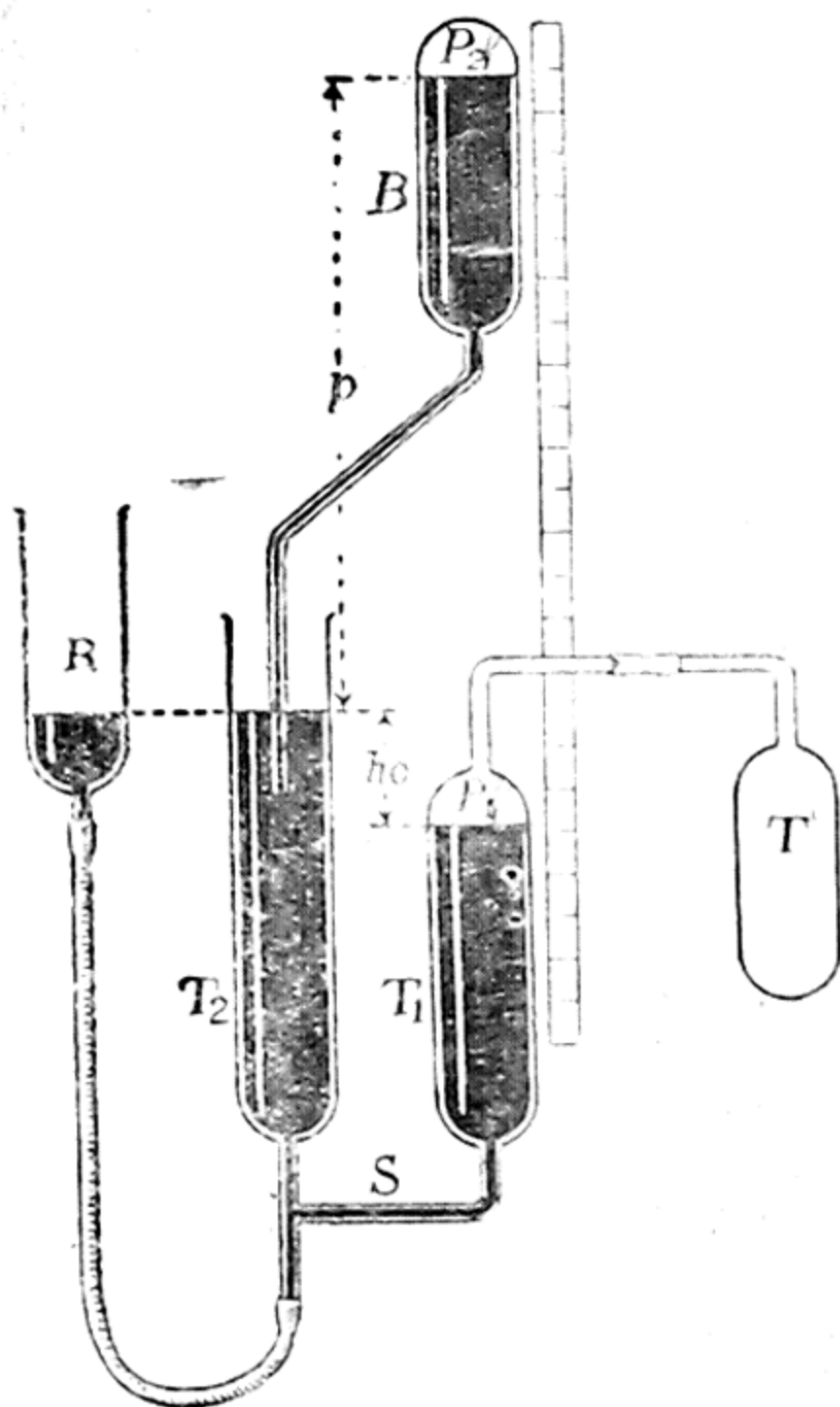


Fig. 1.6.
Hydrogen Thermometer.

¹ A glass bulb may be used upto 500°C, glazed porcelain may be used upto 1000°C, quartz may be used upto 1300°C. Beyond that we use Platinum-Rhodium alloy.

This ensures that the volume of the gas in T always remains constant and all the gas remains *practically* in the bulb T throughout (the volume of the capillary tube and of the space above T_1 is less than 1 c.c.)

To use the instrument, T is surrounded with ice and the level of R is adjusted till the mercury in T_1 just touches P_1 . To determine the corresponding pressure due to the gas in T *directly*, a barometer B is incorporated in the instrument itself. The tube T_2 is joined to T_1 with a steel cross-piece S and the barometer tube is bent so that B is vertically above T_1 . To measure the pressure, B is raised or lowered by means of a vernier-screw till the top of mercury in it just touches the ivory tip P_2 ; the vertical distance P_1P_2 , which can be read off the scale, is the pressure $P_0 = p + h$, due to the enclosed gas, at 0°C . The bulb T is next surrounded with steam at $t^\circ\text{C}$, the corresponding pressure, P_t , is similarly determined.

Next, the pressure P_x , corresponding temperature x is similarly determined. Then

$$x = \frac{P_x - P_0}{P_t - P_0} \cdot t$$

Some corrections have to be applied; because (i) the gas in the dead space above T_1 is not raised to the temperature of the bulb, (ii) there is a slight increase in the volume of the bulb when it is heated.

This thermometer possesses several advantages.

(1) It has a wide range and can be used from the liquefaction point of the gas used, upto about 1500°C .

(2) It is very sensitive because the expansion of gases is considerable. Even if the expansion of the material of the bulb be not quite regular, it will not produce any appreciable error, because the expansion of solids is very much smaller.

(3) Unlike mercury thermometers, two properly-constructed gas thermometers will always agree in their readings, because (i) it is so easy to obtain pure gases and (ii) because the irregularities in the expansion of the bulb have no appreciable effects. This is a considerable and a decided advantage.

(4) Its readings agree closely with the Thermodynamic Scale which is the ultimate standard of reference and which depends upon the properties of no one substance in particular.

The thermometer is, however, unwieldy and on account of the huge size of its bulb it cannot be used for measuring temperatures directly. *It serves as a standard of reference for testing the accuracy of the more convenient and compact thermometers.*

1.12. Platinum Resistance Thermometer. It is due to Siemens and is based on the fact that *the resistance of a piece of pure platinum¹ wire increases continuously as its temperature is raised.* Platinum is an especially suitable material for resistance thermometry because of

¹ Copper resistance thermometers are suitable for measurement of temperatures upto about 100°C . For copper, the resistance-temperature curve is linear, but the low resistance of copper is a serious disadvantage. Nickel is a cheap substitute for platinum upto 300°C .

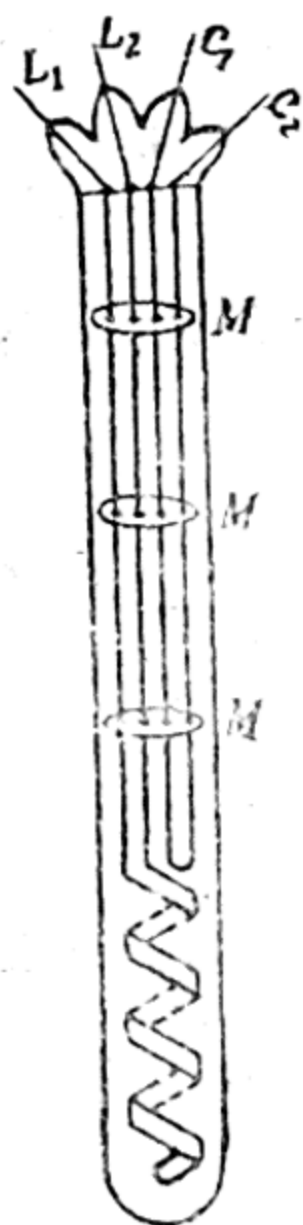
its stability and because the resistance-temperature relationship is so simple. Callender has shown that for wires of pure platinum, the resistance at any temperature t is given by the formula

$$R_t = R_0(1 + \alpha t + \beta t^2) \quad \dots \dots \dots (i)$$

where

t° = temperature as the gas scale, R_0 = resistance of the wire at 0° on the gas scale and α and β are constants.

A piece of pure platinum wire is doubled and wound on a mica



frame. (The wire is doubled to avoid the effects due to self-induction.) The mica frame is enclosed in a tube made of pyrex glass, fused quartz, nickel or porcelain and having *thin* walls. To enable the resistance of the platinum wire to be determined, it is joined to long copper wires L_1 and L_2 called *leads*. To prevent the oxidation of the wires at high temperatures, the tube is exhausted and sealed.

To determine an unknown temperature t , we must know the three constants R_0 , α and β in (i). To determine these, the resistance of the thermometer is determined at

- (1) the melting point of ice *i.e.*, 0°C .
 - (2) the boiling point of water *i.e.*, 100°C
 - (3) the boiling point of pure sulphur *i.e.* 444.6°C ,
- by a modified form of a wheatstone wire-bridge (as given below).

It will be noticed that the leads L_1 and L_2 are necessarily long and have appreciable resistance and this resistance will change with temperature and introduce errors. To eliminate the resistance of the leads, Callender put *compensating leads* C_1 and C_2 of the same material, length and cross-section as L_1, L_2 , in the tube, close and parallel to L_1, L_2 and kept the four wires L_1, L_2, C_1, C_2 separated from one another by passing them through mica discs M, M, M .

Callender and Griffith's Bridge. The ratio arms were made equal, L_1, L_2 were connected in the X arm while C_1, C_2 were put in the R arm. In this case, the resistance of L_1, L_2 will always be balanced by that of C_1, C_2 at all temperatures and will not enter into calculations. A piece of platinum wire EF of uniform cross-section and of resistance k ohms per centimeter was inserted between R and X as shown. If a balance point is obtained at D then

$$R + a.k = X + b.k \quad (\because P = Q)$$

or

$$X = R + (a - b)k$$

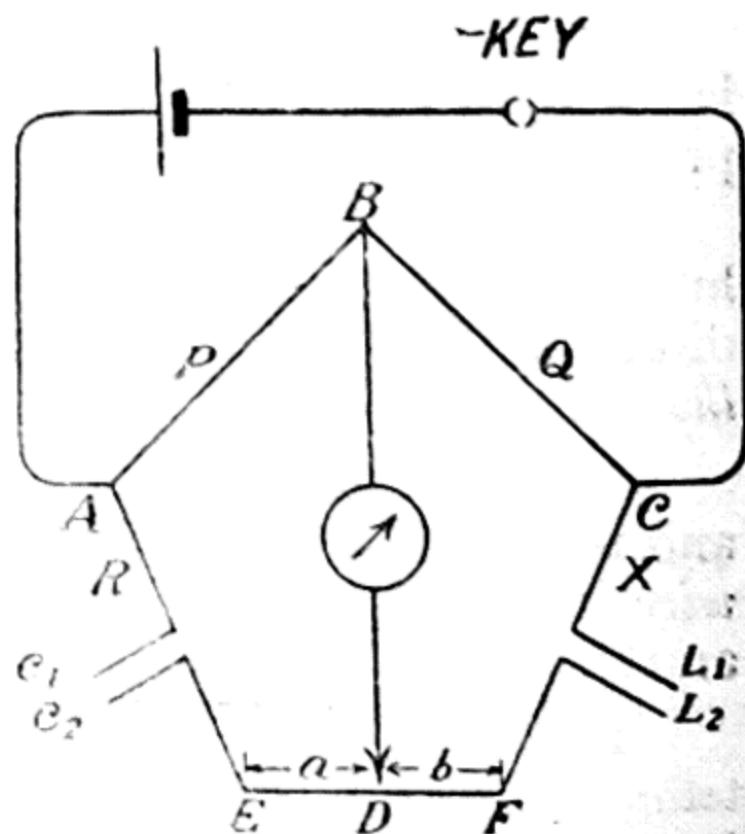


Fig. 1.8.
Callender Griffith Bridge.

The introduction of the wire EF in the bridge makes the balancing very delicate and increases the accuracy of the work.

It is a very compact and neat arrangement and can be used to measure temperatures over a very wide range ($-200^{\circ} \rightarrow 1200^{\circ}\text{C}$) with the accuracy of the standard gas thermometer and hence is a reliable standard. Moreover it has been shown to be free from changes of zero point, because pure, soft, annealed platinum wire has always the same resistance at the same temperature. A resistance thermometer is particularly useful when small temperature changes have to be measured or when the average temperature of a small region is required.

Since the porcelain sheath is not a good conductor, the thermometer cannot quickly attain the temperature of the bath in which it is immersed and in addition possesses a large thermal capacity. Hence *this thermometer cannot measure accurately rapidly-changing temperatures* and is inferior to the thermo-electric thermometer for such purposes.

1.13. Callender has given the following method of calculating temperatures with the help of the platinum resistance thermometer.

On the *platinum scale* of temperature we assert that equal changes in the resistance of the wire denote equal changes in temperature. Thus if R_0 is the resistance at the ice-point, R_{100} at the steam point and R_t at a temperature t_p , then as in a gas-thermometer

$$t_p = \frac{R_t - R_0}{R_{100} - R_0} \times 100 \quad \dots (i)$$

when t_p is a temperature measured on the platinum scale. This temperature is different from the corresponding temperature t , which would be indicated by a gas thermometer. Callender has, however, shown that the difference

$$t - t_p = \delta \left[\left(\frac{t}{100} \right)^2 - \frac{t}{100} \right]$$

where δ is a constant for the particular wire. To determine δ , we find the boiling point t_p of pure sulphur boiling under standard pressure with the help of the platinum resistance thermometer. But we know that sulphur boils at 444.6°C . Substituting these values in (i) δ is determined once for all for that thermometer and any temperature measured on the platinum scale can be easily converted to the gas scale.

It is more convenient to use the linear formula (i) than to use the parabolic formula of the previous article.

1.14. Some Important Fixed Points.

B. P. of Oxygen	...	-182.97°C
M. P. of ice	...	0.00°C
B. P. of water	...	100.00°C
B. P. of sulphur	...	444.60°C
M. P. of silver	...	960.8°C
M. P. of gold	...	1063.0°C

1.15. Seebeck Effect.

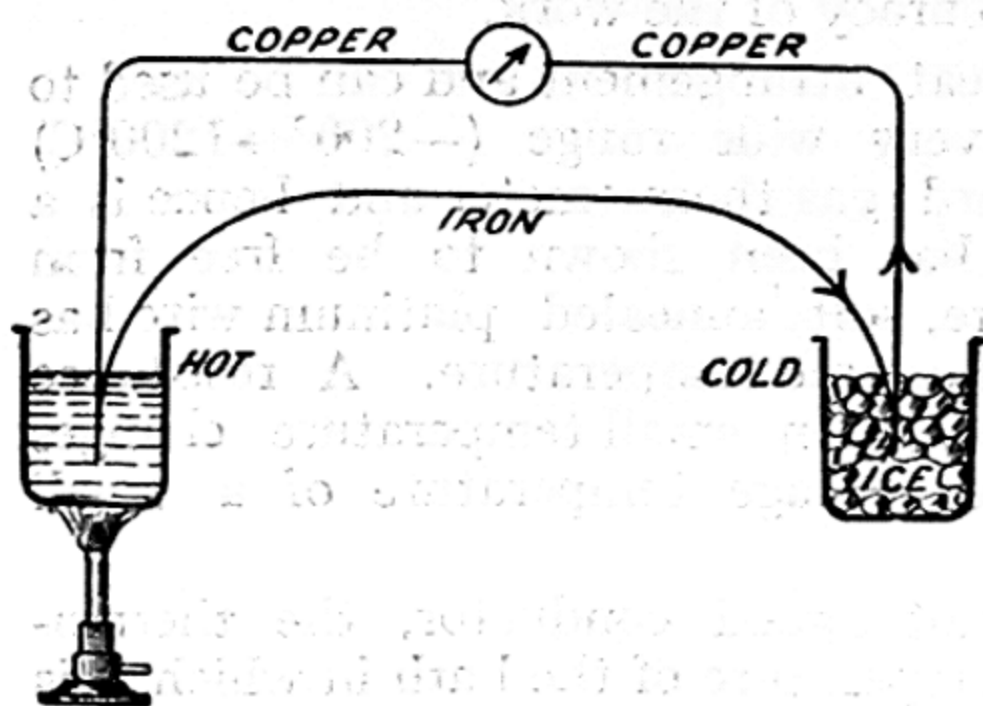


Fig. 1.9.
Thermo-couple.

If two rods of dissimilar substances, say iron and copper, be soldered at the ends so as to form a closed circuit and if while keeping the temperature of one junction constant (say in melting ice) the temperature of the other junction be gradually raised, an e.m.f. is developed in the circuit and a current flows. A galvanometer included in the circuit will indicate a flow of current, while a milli-voltmeter will indicate the e.m.f. developed. The two rods are said to form a *thermo-couple* and the current flowing is the circuit in

called a *thermo-electric current*.

The strength of the current flowing through such a circuit depends upon

- (1) the nature of the materials forming the couple,
- (2) the difference of temperature between the two junctions.

As the temperature of the hot junction is gradually raised, the strength of the current also shows a progressive increase. It is, however, preferable to measure the e.m.f.s. developed in the circuit rather than the currents because the e.m.f. depends only on the temperature and is independent of the resistance of the circuit, while the current depends upon the resistance and the resistance changes with a change of temperature.

As the difference of temperature between the two junctions increases, the e.m.f. also shows a corresponding increase, becomes a maximum for a particular temperature OT of the hot junction (which is different for different couples). With a further increase in the temperature of the hot junction, the e.m.f. begins to decrease and becomes zero for the temperature OS and then changes sign. The temperature OT is called the **Neutral Temperature** for the pair, while OS is the **temperature of Inversion**.

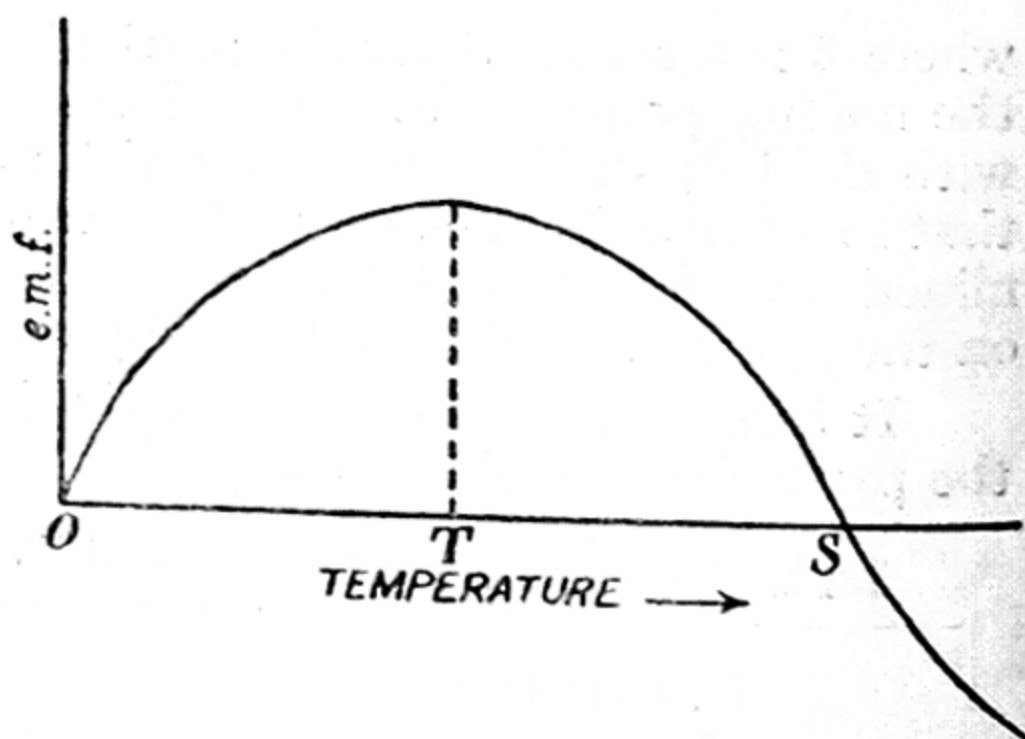


Fig. 1.10.
To illustrate Seebeck Effect.

The neutral temperature is a fixed temperature for a given pair and does not depend on the temperature of the cold junction.

E.M.F's developed with various couples

Temperature°C	E.M.F. developed (milli-volts)				
	Cu-cons- tantan*	Fe-cons- tantan	Pt-cons- tantan	Cu-Plati- num	Pt— Pt. Rh.
—200	—5.54	—8.27	+5.35	—0.19	...
—100	—3.35	—4.82	+2.98	—0.37	...
0	0	0	0	0	0
100	+4.28	+5.40	—3.51	+0.76	+0.642
200	+9.28	+10.99	—7.45	+1.83	+1.45
400	+20.86	+22.07	—16.19	+4.68	+3.25
600	...	+33.27	—25.47	+8.34	+5.22
1000	...	+58.22	—43.92	+18.20	+9.57
1600	+16.67

* Constantan is Cu 60% ; Ni 40%.

1.16. Thermo-electric Thermometer. The e.m.f. developed on establishing a difference of temperature between the two junctions of a thermo-couple is made the basis of temperature measurements. A thermo-electric thermometer consists of three main elements :—

(1) The thermo-couple consisting of two dis-similar metals, usually wires, electric insulation and a protecting tube.

(2) Lead wires to connect thermo-couple and measuring instrument.

(3) The e.m.f. measuring instrument is usually a potentiometer (for great accuracy) and a millivoltmeter (for quick work) *e.g.*, for measuring rapidly changing temperatures. The materials selected for a thermo-couple should develop a relatively large e.m.f. and to ensure freedom from reversal of e.m.f., the neutral temperature should be remote from the temperature-range in use.

The copper-constantan and iron-constantan couples are extensively used for temperature measurements upto 300°C both in the laboratory and in industrial processes. They develop relatively high e.m.f's. and have approximately linear temperature—e.m.f. curves. This is a desirable characteristic since measurements at only a few temperatures serve to establish the calibration curve for the couple. Pt—Pt. Rh couple can be used upto 1600°C. It must be very well-protected because it gets easily contaminated. For temperatures upto 600°C pyrex tubes are very satisfactory for protection as well as insulation. Above 600°C porcelain tubing should be used.

Where however there is no risk of contamination, a thermo-couple can be inserted into the source without a protecting sheath.

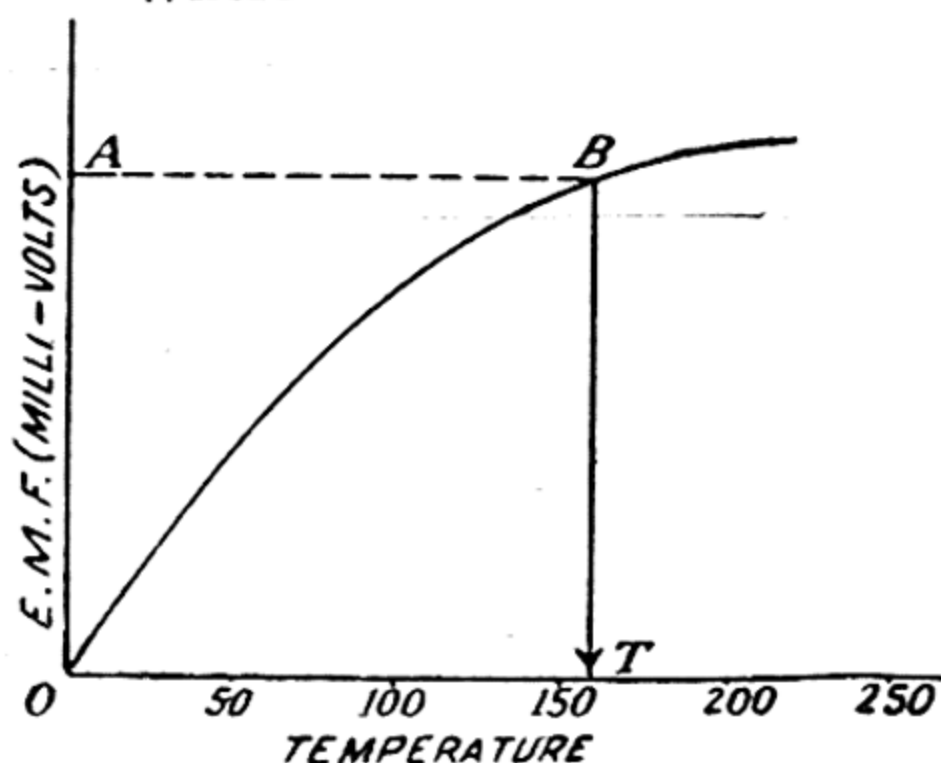


Fig. 1.11.

Temp-e.m.f. curve.

The time-lag between the insertion of the couple and the indication of e.m.f. is then small and it can therefore quickly register varying temperatures. Its small thermal capacity is also a great asset in this case.

In designing a thermoelectric thermometer the following points must be kept in view :—

- (1) The circuit should have a high resistance, so that the change of resistance with temperature may not appreciably affect the voltmeter reading.
- (2) The wires forming the couple should be fairly long, so that when one junction is heated, the other ends of the wires where the voltmeter or galvanometer is joined may remain at practically one constant temperature.
- (3) The portions of the couple at the hot end should be protected in porcelain sheaths to save them from contamination. If there is no such risk the sheaths may be dispensed with.
- (4) The thermo-couple circuit should be properly insulated, as even a slight leakage will produce an appreciable error.
- (5) The e.m.f. in a thermo-couple changes if the wires get strained. Hence great care should be taken in using the instrument.
- (6) Stray e.m.fs. arising from various metallic contacts in the circuit should be guarded against.

Use of Potentiometer.

CE is a platinum wire of length l having a resistance R in series with it. Other connections are made, as shown. If the balance point occurs at D , the fall of potential is proportional to ' a ' and is also proportional to the e.m.f. developed in the thermometer. Let E be the e.m.f. of the cell (this can be measured with a voltmeter) and k , the resistance per cm. of the wire CE . Then the P.D. be-

tween C and $D = \frac{ka}{R+kl} \cdot E$ and can be easily calculated.

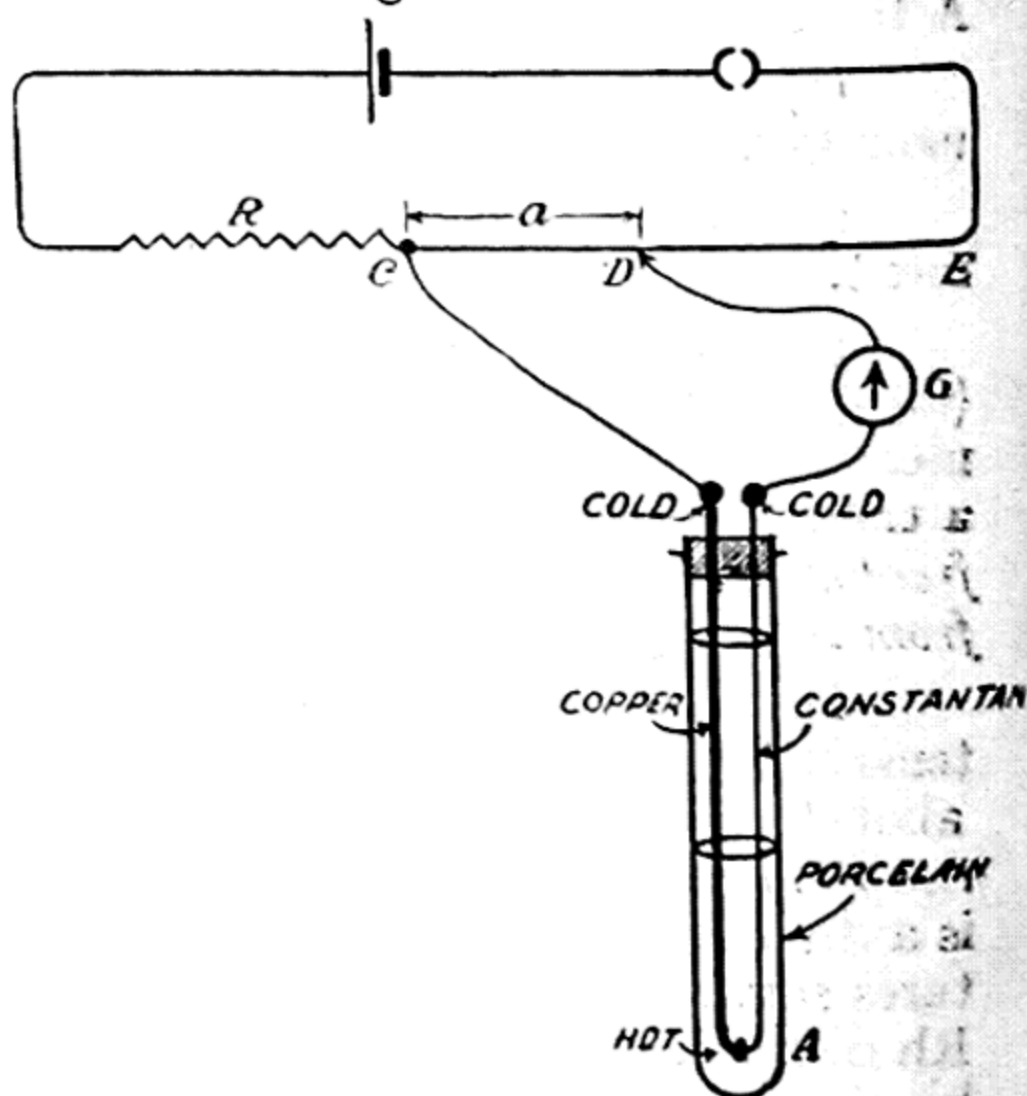


Fig. 1.12.

Use of a couple and potentiometer.

The thermometer is put in a bath which is brought to various known temperatures and the corresponding e.m.f.s. developed are calculated from the position of the balance point *D* in every case. A curve similar to Fig. 1.11 is then drawn. To determine any unknown temperature, the e.m.f. (*OA*, Fig. 1.11) is determined; then *T* gives the corresponding temperature.

For industrial purposes, a milli-voltmeter graduated to read temperatures directly is used with the couple. The instrument then becomes direct-reading, which is a great convenience.

This instrument has a range equal to that of the platinum resistance thermometer but is inferior to it in accuracy. However, for temperatures exceeding 1000°C, it is the only instrument that can be used conveniently. Moreover, it is very well-adapted for measuring varying temperatures due to its low thermal capacity and small time-lag.

In comparison with resistance thermometers, thermo-couples are usually simpler to make, easier to inspect and less difficult to maintain. Usually cheaper to buy, they are generally preferred wherever they meet the requirements of range, sensitivity and accuracy. In addition, the use of couples is sometimes dictated by space requirements.

Using a string galvanometer as indicator, the thermo-couple has been used to study the very rapid temperature variations which occur in a nerve along which a stimulus is being transmitted.

1.17. Electric-power plants depend on temperature-measuring equipment for protection against over-heating and for determining the maximum load that can be safely put on them. To prevent over-heating of motors and generators an automatic recorder and an alarm are necessary. Thermo-couples and Resistance-thermometers are used for the purpose. Sometimes the resistance of the field-winding itself is measured by a sensitive bridge. As the resistance of the coil varies with its temperature, it serves as an index of that temperature.

1.18. Vapour-pressure Thermometers. The pressure of a saturated vapour in equilibrium with its pure liquid varies rapidly with changing temperature. It is possible to utilize this property for temperature measurements. It is actually being employed to good advantage at very low temperatures. The relation between vapour-pressure, *P*, and temperature, *T*, is represented by

$$\log P = A + \frac{B}{T}$$

where *A* and *B* are constants. For greater accuracy, one or more additional terms may be added on the right. Vapour pressure thermometer have distinct advantages in the fact that a great change in vapour pressure corresponds to a comparatively smaller change of temperature. This gives a high sensitivity. Moreover, the vapour pressure is independent of the amount of the liquid present, and of the material, volume and shape of the container. During its liquefaction, a gas can thus act as its own thermometer, right up to its point of liquefaction.

1.19.] Thermistors. Thermistors are devices which have an unusual electrical sensitivity to heat and can detect extremely small temperature-variations (*e.g.*, measuring the warmth of human body from a considerable distance and locating position of a factory-chimney from its heat radiation). They are made of semi-conductors like oxides of manganese, nickel and cobalt. The semi-conductors have the unusual property that their resistance is high when they are cold, but it drops rapidly when they are heated. Thus the resistance of a thermistor, made of oxides of Manganese and Nickel, at 50°C is one-ninth of that at 0°C . Thermistors are usually made by heating the compressed, powdered semi-conductors to a temperature at which they combine into a compact mass. Metal contacts are applied to the mass by firing.

In using a thermistor as a temperature-measurer (and they have other important uses *e.g.*, as voltage regulators, resistance compensators in electrical circuits, speech-volume limiters etc.), the usual electrical-bridge method is adopted. Care is taken that the bridge-current is sufficiently small so that it produces no appreciable heating. If this precaution is taken, the thermistor resistance will depend only on the temperature to be measured.

One great advantage of the thermistors over the resistance thermometer and the thermo-couple is that the associated measuring instruments can be kept at a distance from the hot body whose temperature is being measured, because we can design thermistors of such high resistance that the resistance of the connecting wires can be neglected. It can also detect temperature-changes which are too small to be detected by the other thermometers. Moreover, the temperatures of objects which are inaccessible or are in motion, or are too hot for contact thermometry, can be determined by focussing the radiations from the object on a suitable thermistor.

With the new heat-sensitivity provided by thermistor, it is possible to device bolometers to detect the small heat radiated by such non-incandescent objects as vehicles and ships. The tiny thermistor-element is placed at the focus of a parabolic reflector which is pointed towards any specific object in the same way as the reflector of an astronomical telescope.

QUESTIONS

1. Describe a platinum resistance thermometer. What are its merits and demerits? Give a method of measuring temperatures with it.
2. Give the construction of a thermo-electric thermometer and compare its performance with a standard gas thermometer. What precautions should be taken in measuring temperatures with this instrument.
3. Compare the performance of a gas thermometer, a resistance thermometer and a thermo-couple with one another.
4. What properties are desirable in a thermometric substance. Hence discuss the suitability or otherwise of the thermometric properties of the substances used in the various thermometers.
5. Write short notes on :—
 - (i) Callendar's compensated thermometer.
 - (ii) Vapour pressure thermometer.

- (iii) See-beck effect and its use as a temperature-measurer.
- (iv) Thermistors and their use as temperature-measurers.
- (v) Callendar-Griffith Bridge.
- (vi) Beckmann thermometer.

6. What are the merits of a gas thermometer over the liquid thermometers.

Explain the construction and working of a Jolly's air thermometer. Point out the sources of error in it and suggest some method of removing these objections.

7. Briefly describe a method of measuring temperatures by means of a resistance thermometer. How can temperatures on the gas scale be determined by this thermometer.

8. Discuss the statement 'Heat is energy that flows in response to a temperature-difference.'

9. Write a short historical note on temperature measurements.

CHAPTER II

THERMAL EXPANSION

The difference between the mere curiosity of a child and the developed curiosity of the scientist is that the scientist is no longer interested in isolated facts, but in the grouping of these isolated facts into general conclusions—*Thouless*.

2.1. With very few exceptions (*e.g.*, water below 4°C, and crystals of silver iodide) all substances—solids, liquids and gases—expand when heated. This expansion, though very small, plays an important part in many scientific and everyday problems.

2.2. Expansion of Solids. Solids possess a size and a shape of their own *i.e.*, they have a length, a breadth and a thickness. When heated, expansion takes place in all the three directions. In the case of a thin rod with a comparatively longer length, the increase in length is the more important and is called *linear expansion*. The increase in area is called *superficial expansion* and that in volume, the *cubical expansion*.

(1) **Linear Expansion.** The increase in the length of a rod depends upon (i) its original length, (ii) on the rise of its temperature and (iii) on the nature of its material or

$$L_t - L_0 = L_0 \cdot \alpha \cdot t,$$

where L_t and L_0 are the lengths of the rod at t° and 0° respectively and α is a constant depending on the nature of its material and is different for different materials.

This gives $L_t = L_0 (1 + \alpha t)$

and
$$\alpha = \frac{L_t - L_0}{L_0 \cdot t} = \frac{1}{l} \cdot \frac{dl}{dt}, \quad \dots\dots (i)$$

where dl is the increase in length for a small rise of temperature, dt .

Equation (i) gives the length of a rod at t° , if length at 0° is known. Generally we do not measure the expansion of a rod with respect to its length at 0° . If the length at t_1° is known, that at t_2° is easily determined. Thus $L_{t_1} = L_0 (1 + \alpha t_1)$ and $L_{t_2} = L_0 (1 + \alpha t_2)$

$$\begin{aligned} \therefore \frac{L_{t_2}}{L_{t_1}} &= \frac{(1 + \alpha t_2)}{(1 + \alpha t_1)} = (1 + \alpha t_2) (1 + \alpha t_1)^{-1} \\ &= (1 + \alpha t_2) (1 - \alpha t_1) \\ &= 1 + \alpha(t_2 - t_1) \end{aligned}$$

The increase suffered by a rod one cm. long for a rise of temperature of one degree centigrade is called its coefficient of linear expansion (α). Its value is different for different materials.

(2) **Cubical Expansion.** The increase in the volume of a solid depends (i) on its original volume, (ii) on the rise of its temperature and (iii) on the nature of its material

or

$$\begin{aligned}
 V_t - V_0 &= V_0 \cdot \gamma \cdot t \\
 \gamma &= \frac{V_t - V_0}{V_0 \cdot t} \\
 &= \frac{1}{V} \cdot \frac{dV}{dt}
 \end{aligned}$$

The increase in volume suffered by a cube of one cm. side for a rise of temperature of one degree centigrade is called its coefficient of cubical expansion (γ). Its value is different for different materials.

It is easy to establish a relationship between α and γ . Let l_0 be the length of a solid cube, t the rise of temperature and $\alpha_1, \alpha_2, \alpha_3$ the coefs. of linear expansion along its three sides. Its original volume is $l_0 \times l_0 \times l_0 = l_0^3$. On heating, its three sides become respectively $l_0(1 + \alpha_1 t)$, $l_0(1 + \alpha_2 t)$, $l_0(1 + \alpha_3 t)$ and the volume

$$\begin{aligned}
 V_t &= l_0^3 (1 + \alpha_1 t)(1 + \alpha_2 t)(1 + \alpha_3 t) \\
 &= l_0^3 [1 + (\alpha_1 + \alpha_2 + \alpha_3)t + (\alpha_1 \alpha_2 + \alpha_2 \alpha_3 + \alpha_1 \alpha_3)t^2 + \alpha_1 \alpha_2 \alpha_3 t^3] \\
 &= l_0^3 [1 + (\alpha_1 + \alpha_2 + \alpha_3)t]
 \end{aligned}$$

neglecting the other terms. $\alpha_1, \alpha_2, \alpha_3$ being very small, quantities involving their products will be still smaller and hence negligible.

The increase in volume $V_t - V_0 = l_0^3 (\alpha_1 + \alpha_2 + \alpha_3)t$

$$\therefore \gamma = \frac{V_t - V_0}{V_0 \cdot t} = \alpha_1 + \alpha_2 + \alpha_3$$

In the case of an *isotropic* solid i.e., a solid whose properties are the same in all directions $\alpha_1 = \alpha_2 = \alpha_3 = \alpha$, hence $\gamma = 3\alpha$ or the coefficient of cubical expansion is thrice the coefficient of linear expansion. Crystals generally expand differently along their three axes.

2.3. Change of density with temperature. Let M be the mass of a substance, ρ_0 its density at 0°C and ρ_t its density at $t^\circ\text{C}$.

Its volume at 0°C is $V_0 = \frac{M}{\rho_0}$ and that at $t^\circ\text{C}$ is $V_t = \frac{M}{\rho_t}$

$$\begin{aligned}
 \therefore \frac{\rho_0}{\rho_t} &= \frac{V_t}{V_0} = \frac{V_0(1 + \gamma t)}{V_0} \\
 &= 1 + \gamma t.
 \end{aligned}$$

$$\begin{aligned}
 \text{or } \rho_t &= \frac{\rho_0}{1 + \gamma t} = \rho_0(1 + \gamma t)^{-1} \\
 &= \rho_0(1 - \gamma t).
 \end{aligned}$$

or as the temperature rises, the density diminishes.

2.4. Measurement of Linear Expansion. An accurate method of measurement is the method of Comparator. A standard rod, usually one metre long and the experimental rod of equal size are placed in double-walled troughs containing water. The former is maintained at a constant temperature, usually that of melting ice while the temperature of the latter can be gradually altered and the expansion measured for various ranges of temperature. Two microscopes with cross-wires in their eye-pieces are mounted vertically on

huge stone blocks. The trough containing the standard rod, is

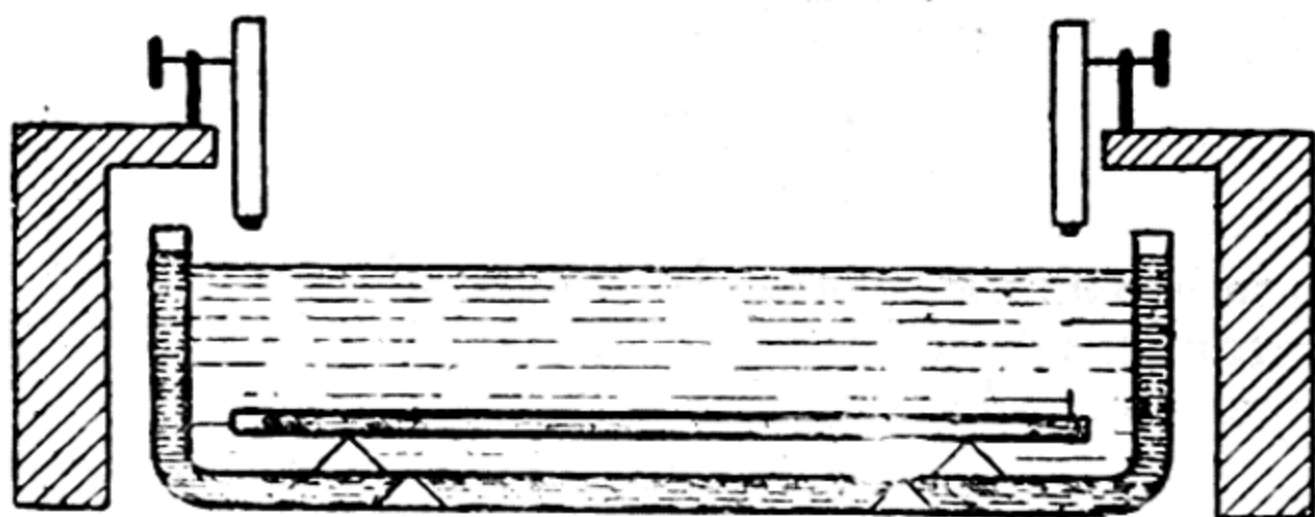


Fig. 2.1.
Comparator arrangement.

brought under the microscopes, and the microscopes are moved backwards or forwards with the help of micrometer screws so that their crosswires coincide with the two fine lines ruled near its ends and the readings of the micrometers are noted. The experimental rod is now brought under the microscopes and the latter are again focussed on fine lines drawn at its ends. The ice-cold water in the troughs is now replaced by water at a known temperature. The rod expands and the microscopes have to be moved backwards to focus them on the lines again. The total distance moved back by the two microscopes is the expansion produced. By changing the water, expansion over various ranges of temperature can be studied. In the end, the standard rod is again brought under the microscopes to make sure that the distance between them has not altered, which is however very unlikely, because they are mounted on massive stones. If, however, there be a slight displacement, a correction has to be applied. For studying the expansion at very low temperatures, the rod can be cooled in liquid air.

The coefficient of expansion of certain nickel-steel alloys is negative (*i.e.*, they contract on heating), while for Invar, at ordinary temperatures, it is practically zero. Hence Invar¹ is used in the construction of watches and clocks. A material 'elinvar' is used for the hair-springs of watches and has the property that its elasticity remains practically constant over a wide range of temperatures. A new variety of Invar which is stainless and inexpandible has also been developed.

A thick-bottomed glass tumbler cracks when heated, due to unequal expansion of its various parts. Pyrex glass which has one-third of the expansion of ordinary glass will not crack in this manner so easily. Silicon, whose coefficient of expansion is one-twentieth of that of ordinary glass may be made red hot and then plunged at once into cold water without cracking.

2.5. Optical lever method for linear expansion. The experimental rod, about 50 cm. in length, is supported centrally in a metal tube lagged with asbestos. The rod is supported against a hard point H at the lower end so that on heating it can expand only upwards. An optical lever is placed with its hind leg on the top of the rod and

¹ Iron containing 36 per cent nickel.

the two front legs resting on a metal block M . A scale and telescope arrangement is set up at a distance of about 1.5 metres from the rod.

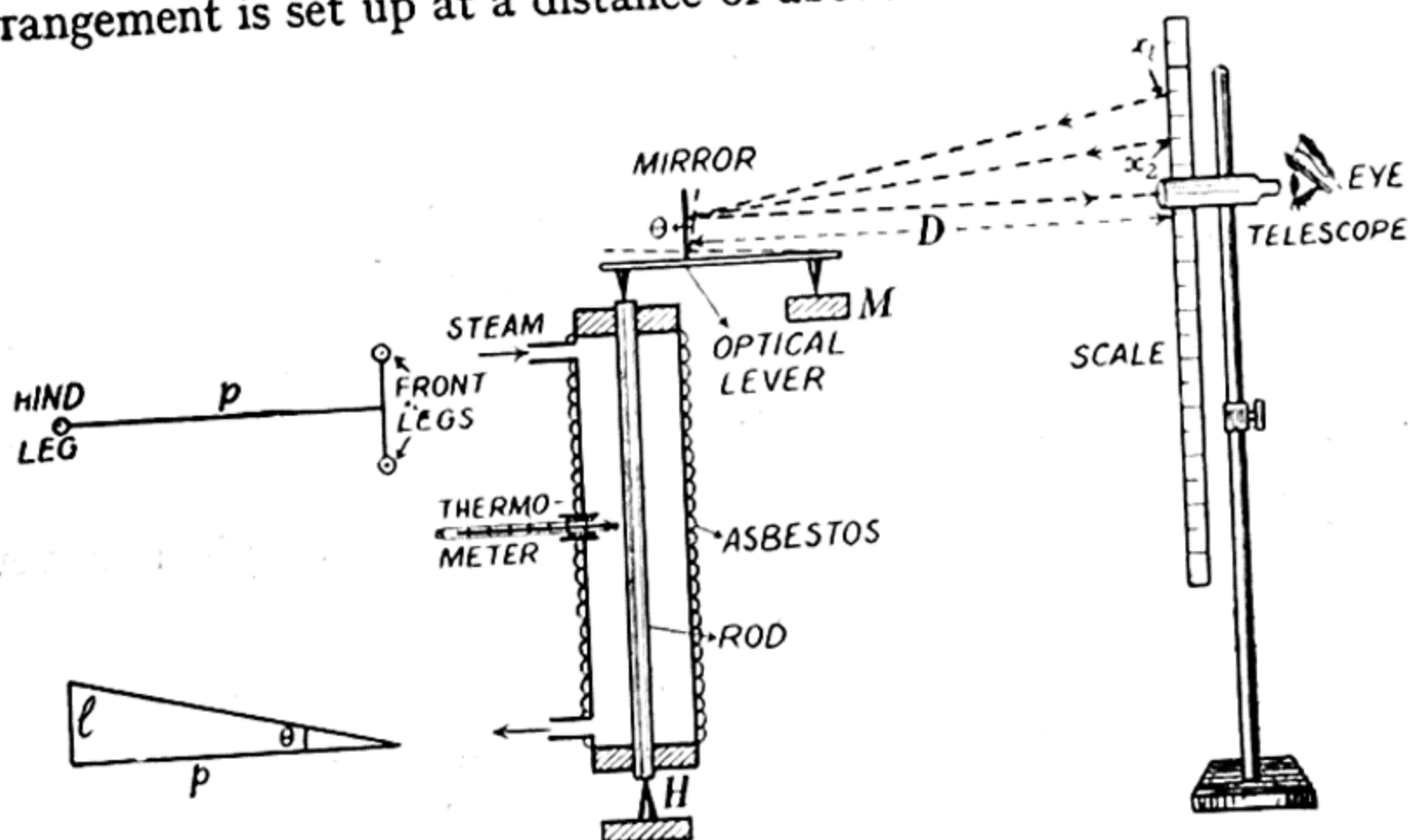


Fig. 2.2.
Optical lever method.

The light from the scale after reflection at the mirror enters the telescope. Suppose the image of x_1 coincides with the horizontal cross-wire of the telescope when the rod is at the initial temperature t_1 , which is given by the thermometer whose bulb touches the rod. Steam is now circulated round the rod, the rod expands upwards and the lever is slightly tilted forward so that some mark other than x_1 now comes on the cross-wires. The position of the mark is read on the cross-wires every two minutes. When the rod is fully expanded, suppose a mark x_2 is on the cross-wire. Let the final temperature be t_2 .

The displacement is $x_1 - x_2 = x$

Let p be the perpendicular distance between the hind leg and the line through the front legs of the optical lever. This can be found by pricking a paper with the lever.

If l be the increase in the length of the rod, the angle θ through which the lever is tilted, is given by

$$\theta = \frac{l}{p}$$

.....(i)

also

$$\tan 2\theta = \frac{x}{D}$$

because when a mirror turns through an angle θ , the reflected ray moves through 2θ . As θ is small

$$2\theta = \frac{x}{D}$$

$$\theta = \frac{x}{2D}$$

.....(ii)

or

combining (i) and (ii)

$$\frac{l}{p} = \frac{x}{2D}$$

$$\therefore l = \frac{px}{2D}$$

The coefficient of linear expansion of the rod is

$$\alpha = \frac{l}{L.(t_2 - t_1)}$$

where L is the original length of the rod.

This is a very sensitive method and is capable of yielding very good results.

Expansion Coefficients.

Aluminium	25.5×10^{-6}
Copper	16.7
Steel	10.5 to 11.6
Platinum	8.9
Brass	18.9
German silver	18.4
Silica	0.5
Hard glass	9.7

2.6. Gruneisen Law. The coefficient of linear expansion of solids changes with temperature ; it decreases as the temperature falls. The specific heat of solids changes in the same way. Gruneisen gave the law that *the ratio of the coefficient of linear expansion of a metal to its specific heat at constant pressure is constant at all temperatures.* This can be seen from the following table.

$t^\circ C$	$\alpha \times 10^6$	$\frac{\alpha \times 10^6}{C_p}$	$t^\circ C$	$\alpha \times 10^6$	$\frac{\alpha \times 10^6}{C_p}$
	Aluminium			Silver	
-100°	18.2	109	-87°	17.1	329
0	23.0	110	0	18.3	327
100	24.9	112	100	19.2	331
300	29	119	500	23.1	350
	Copper			Platinum	
=87°	14.1	174	-100°	7.9	268
0	16.1	177	0	8.9	280
100	16.9	180	100	9.2	277
400	19.3	179	875	11.2	267

It is evident that for any one substance the values in the third column are practically constant.

2.7. Expansion of Crystals. Since crystals are obtainable in small sizes, their expansion on heating, is extremely small and cannot be measured by ordinary methods. Fizeau used the method of *interference of light*¹ for measuring these minute changes of length. The

opposite faces of a crystal are ground plane and parallel to each other. It is then placed on the polished top P of the table. A long-focus lens is placed near and parallel to the surface of the crystal C . The thickness of the air-film between the top of the crystal and lower surface of the lens is adjusted to a suitable small value. The film is then illuminated with a parallel beam of monochromatic sodium light which is reflected down vertically on it by the glass plate G .

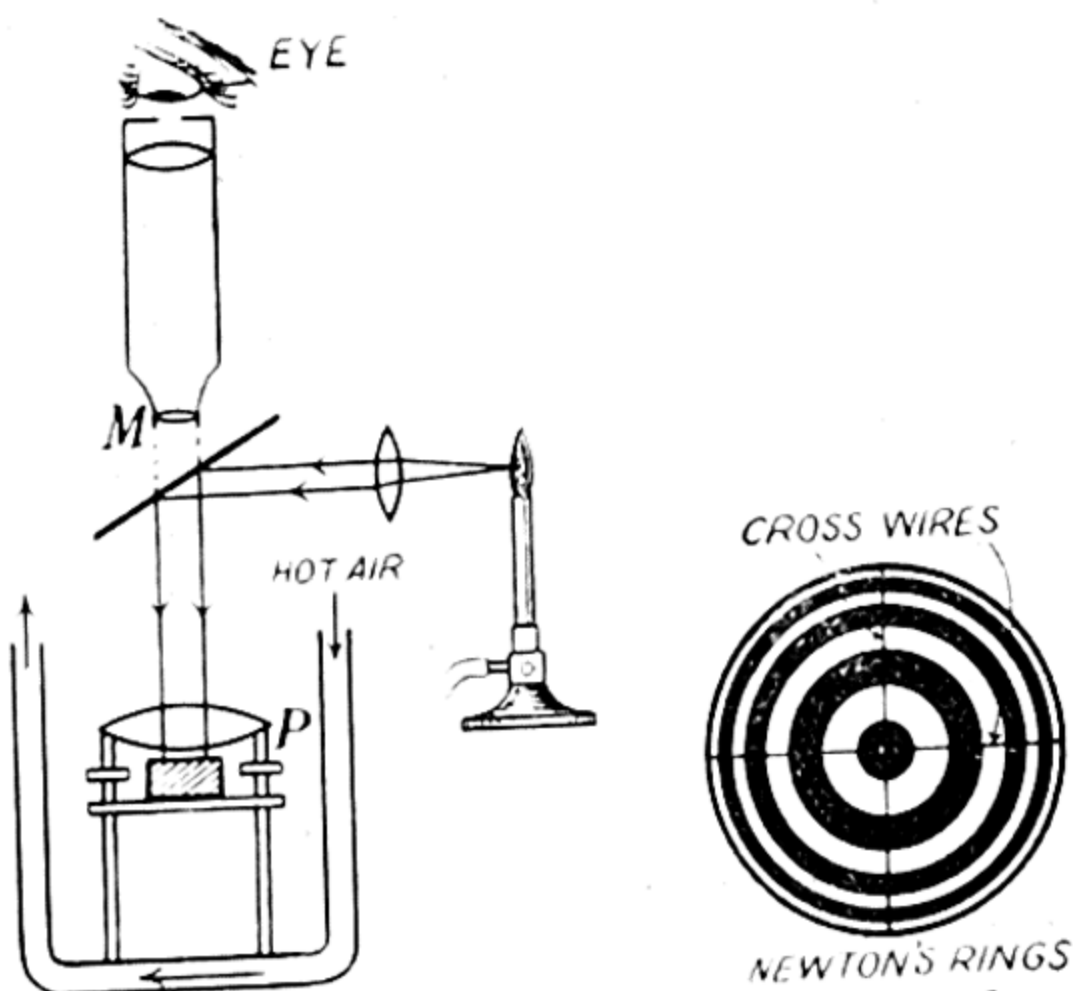


Fig. 2.3. Fizeau's apparatus for crystals.

Interference takes place between the light reflected from the top of the crystal and the lower surface of the lens and a microscope M focussed on the air-film sees a number of alternate bright and dark rings called *Newton's rings*. The temperature of the crystal and the plate P is read by a thermometer placed in contact with them. The apparatus is enclosed in a chamber with double walls in which any desired temperature can be maintained by circulating hot air through the annular space. The crystal expands, the thickness of the film alters and the rings are displaced. The rings expand and move outwards as the thickness of the air-film diminishes. A displacement of one ring corresponds to an alteration in the thickness of air-film equal to half the wave-length of the light used. The rings are counted as they pass across the field of view past a cross-wire. After a suitable number of rings have passed, the heating is stopped and temperature of the crystal is noted again. If n be the number of rings that cross the field of view while the temperature changes from t_1 to t_2 .

¹ According to Huygen light travels in the form of waves. If two waves of equal amplitude and length travel over the same path, the resultant displacement at any point depends upon the phase difference between the waves and is equal to the algebraic sum of the individual displacements. If the two waves agree in phase, they re-inforce each other producing a maximum effect. If they are in opposite phases, they annul each other's effect or interfere destructively and produce a minimum effect. This is known as Interference of Light. Interference is the cause of the formation of Newton's rings.

$$n. \lambda/2 = l_1 a_1 (t_2 - t_1) - l_2 a_2 (t_2 - t_1) \\ = (l_1 a_1 - l_2 a_2) (t_2 - t_1)$$

where l_1 and l_2 are the lengths of the crystal and the supporting screws, a_1 and a_2 their coefficients of expansion and λ is the wave length of the light. The wave-length of the yellow light is 6×10^{-5} cm. and since a displacement equal to $\frac{1}{5}$ th of a ring can be easily measured, expansion of the order of $(6 \times 10^{-5})/5 \times 2$ or 10^{-6} cm. can be measured in the way.

To measure the expansion of the screws, in order to determine the absolute expansion of the crystal, the above experiment is repeated without using the crystal, interference taking place between the polished plate P and the lower surface of the lens.

Tutton improved this apparatus by supporting the crystal on a small three-legged table of aluminium resting on the plate P . The levelling screws are made of platinum. Their relative heights are so adjusted that the expansion of the aluminium table just cancels the expansion of the platinum screws. The absolute expansion of the crystal is thus directly obtained.

The expansion of a crystal is usually different along its three axes. Hence to determine its cubical expansion, the linear expansion coefficients a_1, a_2, a_3 are measured along three mutually perpendicular axes and the cubical expansion determined using the relation

$$\gamma = a_1 + a_2 + a_3.$$

In certain crystals e.g., ice-land spar, a rise of temperature causes a contraction in certain directions while expansion occurs along other directions.

2.8. Real and apparent expansion of a liquid. A liquid possesses a volume only and takes up the shape of the vessel in which it is contained. When the liquid is heated in order to find its volume expansion, the vessel containing it also expands and complicates the problem. Hence in determining the *real* expansion of a liquid, we must know the extent to which the vessel has expanded. If we ignore the latter, we only get the observed or *apparent* expansion.

Suppose the liquid is contained in a graduated flask. Let V_0 be its volume at 0°C and V_1 its *observed* volume at $t^\circ\text{C}$. Then, the coef. of apparent expansion

$$\gamma_a = \frac{V_1 - V_0}{V_0 \cdot t}$$

If g be the coefficient of cubical expansion of the containing vessel, the real volume of the vessel upto the V_1 graduation will be $V_1(1 + gt)$ and the coefficient of *real* expansion

$$\gamma_r = \frac{V_1(1 + gt) - V_0}{V_0 \cdot t} \\ = \frac{V_1 - V_0}{V_0 \cdot t} + \frac{V_1}{V_0} \cdot g$$

$$\begin{aligned}
 &= \gamma_a + \frac{V_0(1+\gamma_a)t}{V_0} g \\
 &= \gamma_a + g + \gamma_a \cdot g \cdot t. \\
 &= \gamma_a + g
 \end{aligned}$$

neglecting the third term. Or,

the coef. of real expansion of a liquid = coef. of apparent expansion + coef of cubical expansion of the containing vessel.

2.9. Determination of coef. of apparent expansion. It can be determined with the help of a specific gravity bottle. The bottle is cleaned, dried and weighed. It is then filled completely with the experimental liquid which is a few degree *above* the room temperature. This is done because the temperature inside a balance-case is always a bit higher than the room temperature and if the bottle were filled with liquid at room temperature, a little of the liquid might escape by expansion while it is being weighed. Next, the bottle is suspended by a wire in a bath, so that it is dipping upto the neck in the bath. The temperature of the bath is raised and then kept constant for sometime at a temperature a few degrees below the boiling point of the experimental liquid. (A water-bath can be used with glycerine). The liquid expands and some of it escapes. The bottle is now taken out from the bath, cooled, dried on the outside and weighed.

Let M be the mass of the liquid left inside at the higher temperature t , m the mass that overflows and let ρ be the density of the liquid. The mass filling the bottle at the lower temperature to is $(M+m)$. It is clear that a volume M/ρ of the liquid expands to $(M+m)/\rho$ for a rise of temp. $(t-t_0)$. Hence coef. of apparent expansion of the liquid is

$$\begin{aligned}
 \gamma_a &= \frac{\frac{M+m}{\rho} - \frac{M}{\rho}}{\frac{M}{\rho} \cdot (t-t_0)} \\
 &= \frac{m}{M(t-t_0)}.
 \end{aligned}$$

or coef. of apparent expansion

$$= \frac{\text{mass of liquid expelled}}{\text{mass of liquid inside at the higher temperature} \times \left\{ \begin{array}{l} \text{rise of} \\ \text{temperature} \end{array} \right\}}$$

2.10. Determination of coefficient of real expansion of mercury (Dulong and Petit's method).

The real expansion of mercury was directly determined by Dulong and Petit in 1817. The determination is based on the principle that *the pressure exerted by a column of liquid depends only on the vertical height of the column and on the density of the liquid and is not affected by the shape and size of the containing vessel.*

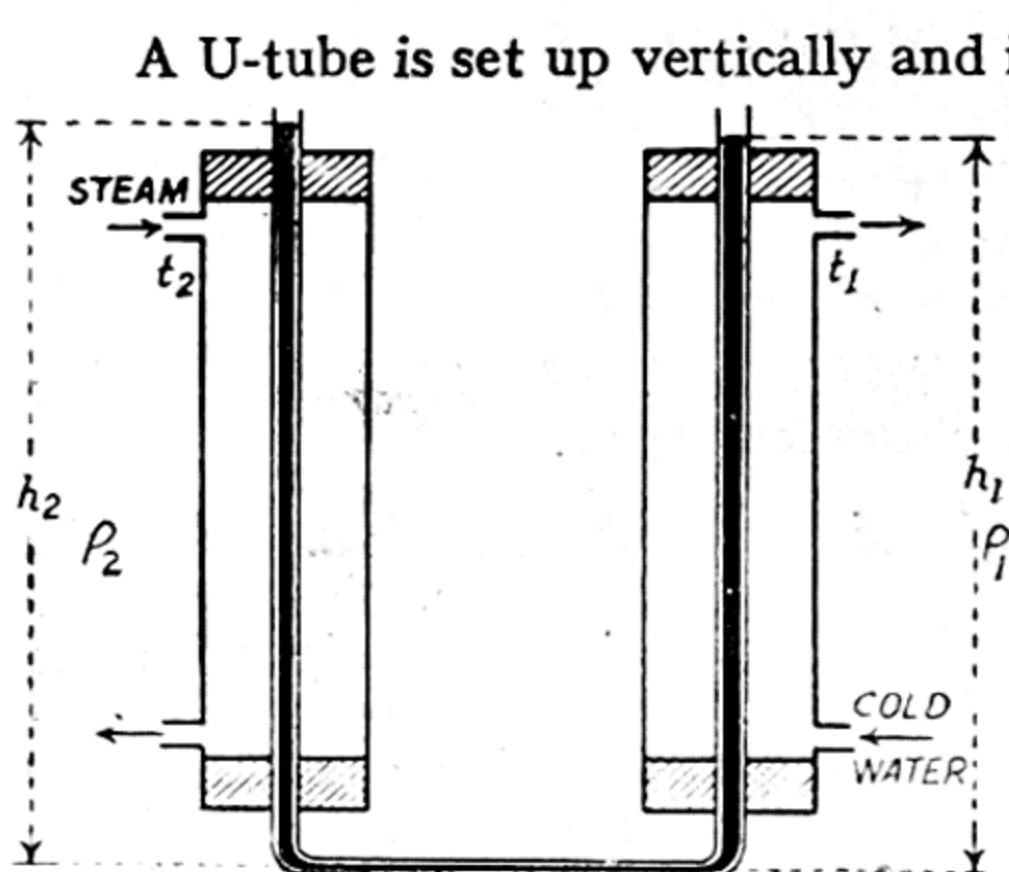


Fig. 2.4.

Dulong and Petit's arrangement.

A U-tube is set up vertically and its central limb is kept horizontal. The vertical limbs are surrounded by wider tubes. Through one tube steam at t_2° , and through the other, cold water at t_1° is passed while the U-tube is filled with mercury. The lengths of the vertical liquid columns are equal to begin with. Later, the mercury in the hot limb expands while that in the cold limb contracts. The two heights h_1 and h_2 are measured after conditions have become steady. Then if ρ_1 and ρ_2 be the densities of mercury at t_1° and t_2° respectively.

$$\frac{\rho_1}{\rho_2} = \frac{1 + \gamma t_2}{1 + \gamma t_1} = \frac{h_2}{h_1} \dots \dots \dots (\text{Art. 2.3})$$

or

$$\gamma = \frac{h_2 - h_1}{h_1 t_2 - h_2 t_1}$$

The above arrangement is not satisfactory because

(i) The liquid above the corks is necessarily at a different temperature from the liquid below.

(ii) As surface tension depends upon temperature, the curvature of the meniscus will be different in the two limbs and this will make the measurement of heights less accurate.

(iii) There will be a convective flow of the liquid along the horizontal tube which will produce a mixing of hot and cold liquids at the lower ends of the vertical limbs. To lessen this error, the horizontal tube was made of a narrower bore.

To overcome these objections, Regnault devised two methods for determining the absolute expansion of mercury or, as a matter of fact that of any other liquid.

Some Expansion Co-efficients.

Methyl Alcohol	122×10^{-5}
Ethyl Alcohol	110
Mercury	18.18
Glycerine	53
Turpentine	94
Sulphuric acid 100 %	57

2.11. Regnault's Determination of Real Expansion.

First Arrangement. Two vertical tubes AB and CD are

connected near their tops by a horizontal tube AC of fine bore having a small hole at L . These tubes are connected at B and D to a bent tube $BEFGHD$ as shown. A branch at K is connected to a pump by means of which air may be forced into FG . The free surfaces at A and C are subject to the pressure of the atmosphere while the surfaces in the tubes EF and GH are subject to an air-pressure sufficient to maintain the levels as shown. The mercury in $CDHG$ and in EF is kept at a constant temperature t_1 and that in AB at a higher temperature t_2 . The hole L ensures that the upper surface of mercury in the vertical tubes is at the same level as L .

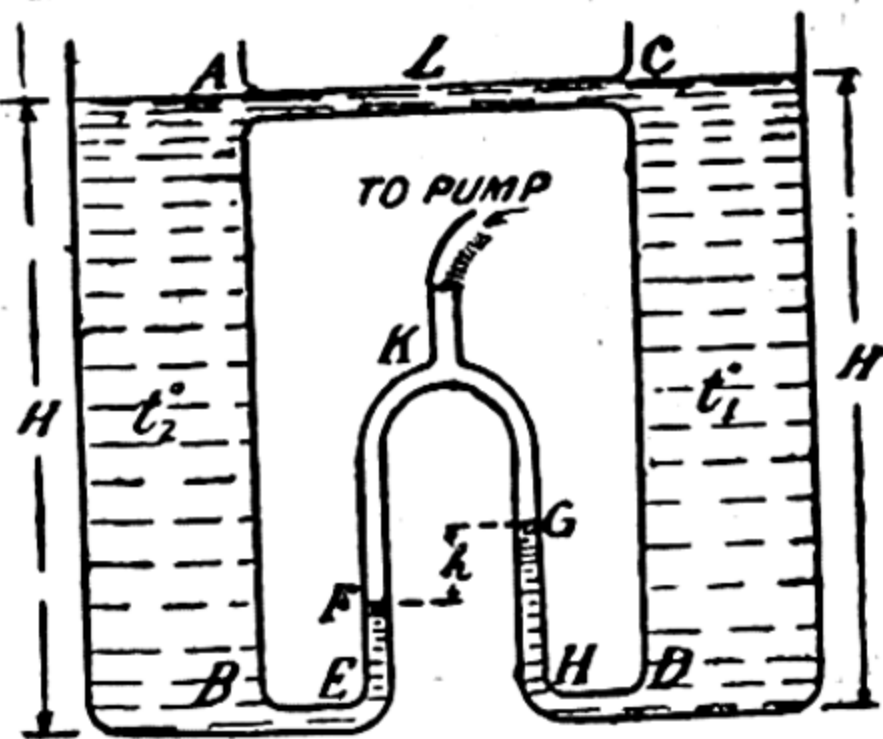


Fig. 2.5.
Absolute of expansion of liquid
Regnault.

Since pressures at A and C , and also at F and G are equal, a column of mercury equal to the vertical height $FG=h$, gives the difference in pressures due to equal columns of mercury, one hot and the other cold. Hence the effective height of the cold column is CD minus the height FG , while that of the hot column is AB or H

$$\therefore \gamma = \frac{1}{t_2 - t_1} \cdot \left(\frac{h}{H - h} \right)$$

Second Arrangement. It consists of two narrow steel tubes AB and CD joined at the bottom by a flexible iron tube F and at the top to glass tubes G_1 and G_2 .

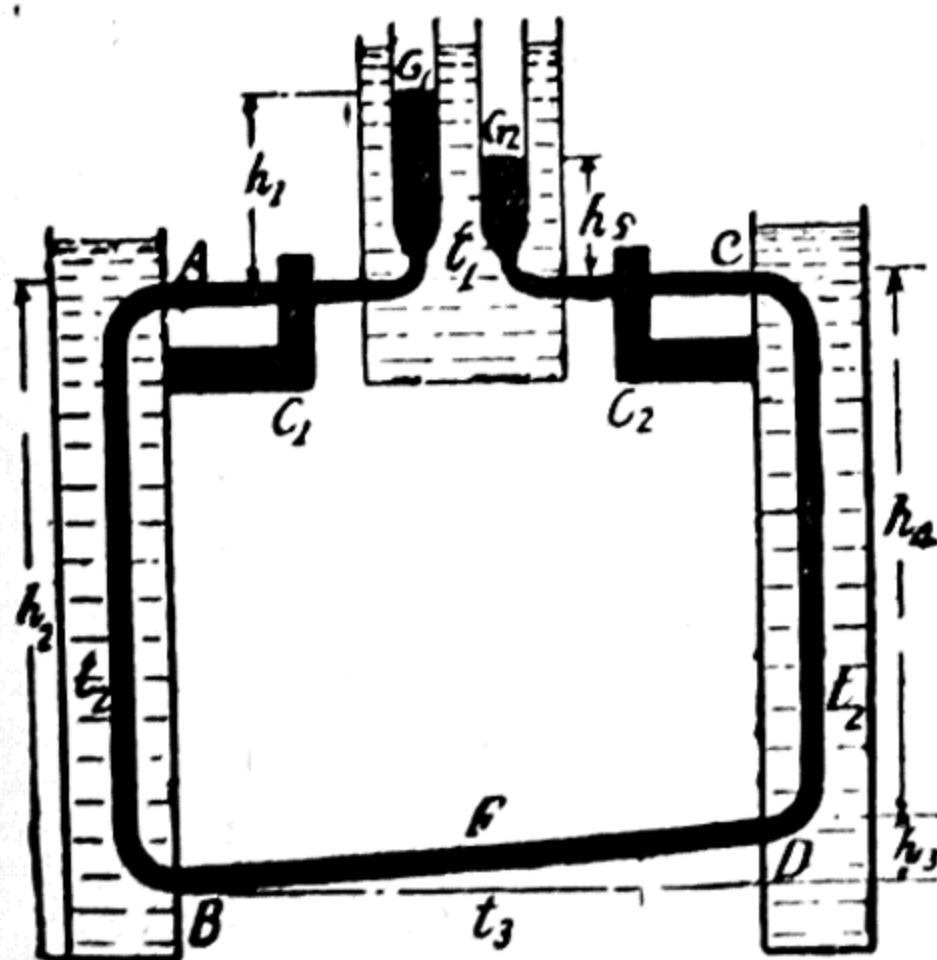


Fig. 2.6.
Regnault's Second Arrangement.

The portions of the steel tubes at A and C are maintained accurately horizontal throughout, with the help of copper blocks C_1 and C_2 . The vessels holding G_1 , G_2 and CD contain water at a common temperature t_1 while AB is surrounded with water, at a higher temperature t_2 . The flexible tube F enables AB to expand and CD to contract freely. As a result of heating AB and cooling CD , B is pushed down while D is pulled up. The mercury in AB expands and therefore stands higher in G_1 , while

that in CD shrinks and stands lower in G_2 .

The pressure at G_1 and G_2 is the same (*i.e.*, atmospheric), hence for equilibrium, the difference of pressures between G_1 and B , must equal that between G_2 and B . If t_3 be the mean temperature of F , it is clear from the diagram that

$$h_1\rho_1 + h_2\rho_2 = h_3\rho_3 + h_4\rho_1 + h_5\rho_1$$

where ρ_1, ρ_2, ρ_3 are the densities of mercury at t_1, t_2, t_3 respectively.

But

$$\rho_t = \frac{\rho_0}{1 + \gamma.t}$$

$$\therefore \frac{h_1\rho_0}{1 + \gamma.t_1} + \frac{h_2\rho_0}{1 + \gamma.t_2} = \frac{h_3\rho_0}{1 + \gamma.t_3} + \frac{h_4\rho_0}{1 + \gamma.t_1} + \frac{h_5\rho_0}{1 + \gamma.t_1}$$

or
$$\frac{h_1}{1 + \gamma.t_1} + \frac{h_2}{1 + \gamma.t_2} = \frac{h_3}{1 + \gamma.t_3} + \frac{h_4}{1 + \gamma.t_1} + \frac{h_5}{1 + \gamma.t_1}$$

from which γ can be calculated. There is some uncertainty about the temperature t_3 , but since h_3 is very small, the mistake introduced is almost negligible.

Two Methods Compared. In the first method the mixing of hot and cold liquids is impossible and since, EF and GH are at the same temperature, the surface tension at the top of these columns is equal. The mercury at A and C is at different temperatures and a mistake in heights is possible due to the unequal surface tension in the two limbs. Since, however, the tubes are very wide, the error is not appreciable. In the second method, the top of mercury columns at G_1 and G_2 is at the same temperature and there is no error due to surface tension, but a mixing of hot and cold liquids does occur in F and there is also some slight uncertainty about the temperature t_3 . The second method has been improved upon by Callendar and Moss and has found favour with other workers also.

2.12. Arrangement of Callendar and Moss. In the Regnault's

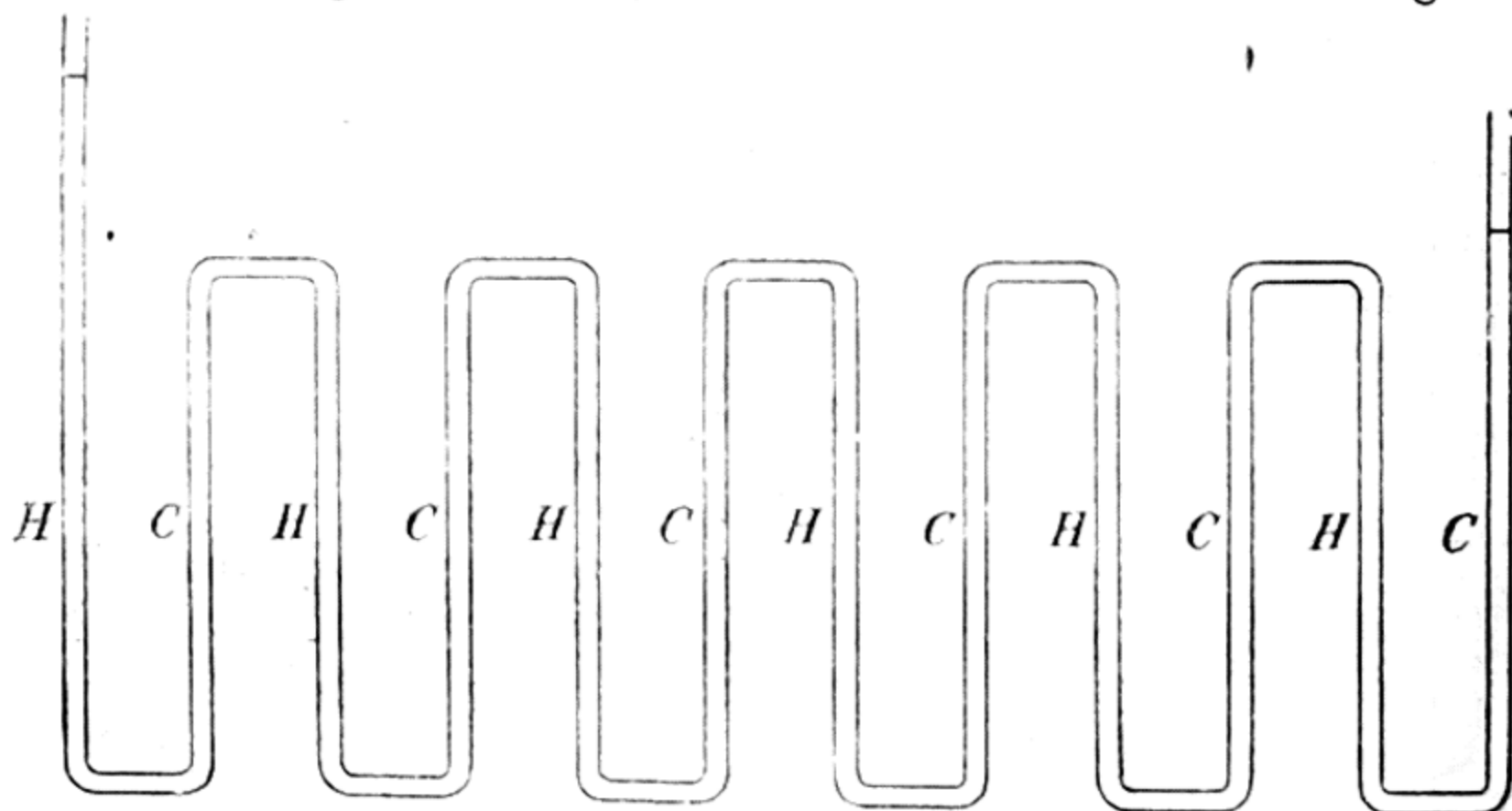


Fig. 2.7.
Callendar and Moss's Arrangement.

In the second arrangement the two mercury columns were each 1.5 metres long. Callendar and Moss used six pairs of hot and cold columns which

were connected in series as shown. The hot columns were arranged side by side and were placed in one bath. Similarly the cold columns were placed in another. This amounts to using a hot and a cold column of six times the length used by Regnault, and the method consists in *increasing the effective length of the two columns and yet keeping the whole arrangement quite compact*. Using this arrangement, they determined the expansion of mercury in various ranges of temperature. The mean value of the expansion of mercury between 0°C and 100°C is 0.000182.

2.13. Expansion of Gases. Although the effect of pressure on the volume of solids and liquids is negligible, it is considerable in the case of gases. Hence in the case of a gas three variable—Pressure, Volume and Temperature—must be considered.

(1) According to *Boyle's law*, the volume of a given mass of gas is inversely proportional to the pressure acting upon it, *provided temperature does not change*. Thus on doubling the pressure, the volume of a gas will be halved. This property is common to all gases.

(2) Again, on heating any gas at *constant pressure*, it is found that it increases in volume by $\alpha = \frac{1}{273.2}$ of its volume at 0°C for each degree centigrade rise of temperature. This is the *Charles's law* for gases.

(3) If the temperature of a gas be raised, while its *volume is kept constant*, it is found that the coefficient of increase of pressure, β is also equal to $\frac{1}{273.2}$.

Careful experiments show that all gases show marked deviations from these laws under trying conditions—neither the volume changes with pressure as postulated by Boyle's law, nor is the expansion the same for all gases as demanded by Charles's law. A gas which would conform to both the above laws rigorously is called an *ideal gas*.

2.14. For an Ideal Gas $\alpha = \beta$. Keep the pressure of a gas constant at p_0 and change its temperature for 0° to $t^{\circ}\text{C}$, the volume will become

$$V_t = V_0(1 + \alpha t)$$

Now, let the gas be compressed to its original volume v_0 , while its temperature is kept at t° . Its pressure will now rise to p_t given by

$$p_t v_0 = p_0 v_t$$

$$p_t = p_0(1 + \beta t).$$

$$p_0(1 + \beta t).v_0 = p_0 v_0(1 + \alpha t)$$

$$1 + \beta.t = 1 + \alpha.t$$

$$\alpha = \beta.$$

also

\therefore

or

or

2.15. General Equation for an Ideal Gas. According to

Boyle's law, volume of a gas is inversely proportional to its pressure at constant temperature

or
$$V \propto \frac{1}{P} \quad \dots \dots \dots (i)$$

According to Charles's law, at constant pressure

$$V_t = V_0 \left(1 + \frac{1}{273.2} t \right) = \frac{V_0}{273.2} (273.2 + t) = a.T$$

where T is the Absolute Temperature corresponding to $t^\circ\text{C}$ and a is a constant $= V_0/273.2$

or generally
$$V \propto T \quad \dots \dots \dots (ii)$$

But an ideal gas obeys both the above laws

$$\therefore V \propto T \cdot \frac{1}{P}$$

or
$$PV \propto T \text{ or } PV = RT \quad \dots (iii)$$

where R is a Constant called the Gas Constant. The equation (iii) is known as the Equation of State for an *Ideal Gas*. No gas is ideal in this sense but the more permanent gases like Oxygen, Nitrogen, Helium etc. can be considered as ideal for all practical purposes. They show marked deviations only at very low temperatures.

2.16. Evaluation of the Gas Constant. If V be the gram-molecular volume *i.e.*, the volume of a gm.-mol. of any gas (*e.g.* of 2.016 gm. of H or 32 gm. of O) we have $P = 76 \times 13.6 \times 981$ dynes, $T = 273.2$ and $V = 22,410$ c.c.—the same for a gm.-mol. of all gases.

$$\therefore 76 \times 13.6 \times 981 \times 22,410 = R \times 273.2$$

or
$$R = 8.31 \times 10^7 \text{ ergs per gm.mol per degree C}$$

This is a universal constant.

If, however, V be the volume of 1 gm. of any gas under normal pressure and at 0°C , the equation is put in the form

$$PV = r.T$$

The value of r is no longer the same for all gases. It changes with the nature of the gas. Thus $V = 700$ c.c. for oxygen and 11,130 for hydrogen.

$$r(\text{Oxygen}) = \frac{(76 \times 13.6 \times 981) \times 700}{273.2}$$

$$= 2.6 \times 10^6 \text{ ergs. per gm. per degree C.}$$

and
$$r(\text{Hydrogen}) = \frac{(76 \times 13.6 \times 981) \times 11130}{273.2}$$

$$= 4.13 \times 10^7 \text{ ergs. per gm. per degree C.}$$

2.17. Thermostat. It is a device for maintaining a bath or any closed space (*e.g.*, the interior of a refrigerator) at any desired temperature for considerable periods, to within about 1°C . If the temperature gets less, the heat input is automatically increased, and if the temperature rises above the desired value, the heat in-put

is automatically diminished. For temperatures upto 100°C , a liquid or a bi-metallic thermostat can be used but from 100° — 300° the later device is usually employed.

(1) *Liquid Thermostat* :—An expanding liquid column gradually restricts the flow of gas to the burner heating the bath. At the desired temperature the supply of gas just keeps the burner lighted and when the liquid is slightly cooled down, the gas-supply gets augmented. The temperature can thus be maintained constant within narrow limits. The tube T is filled with toluene which has a high expansion coefficient, the rest of the arrangement contains mercury. As the temperature of the bath rises, the meniscus of mercury at R moves nearer to the end of the tube delivering the gas to the burner. The quantity of mercury is so adjusted that at the desired temperature the mercury just closes the end R and the gas-supply is cut off. To keep the burner lighted, a by-pass is provided for the gas at S . The supply of the gas at S can be adjusted by pressing the rubber tube by means of the pinch cock. When the temperature of the bath falls a little, the mercury level at R gets lowered and the gas begins to flow out of R .

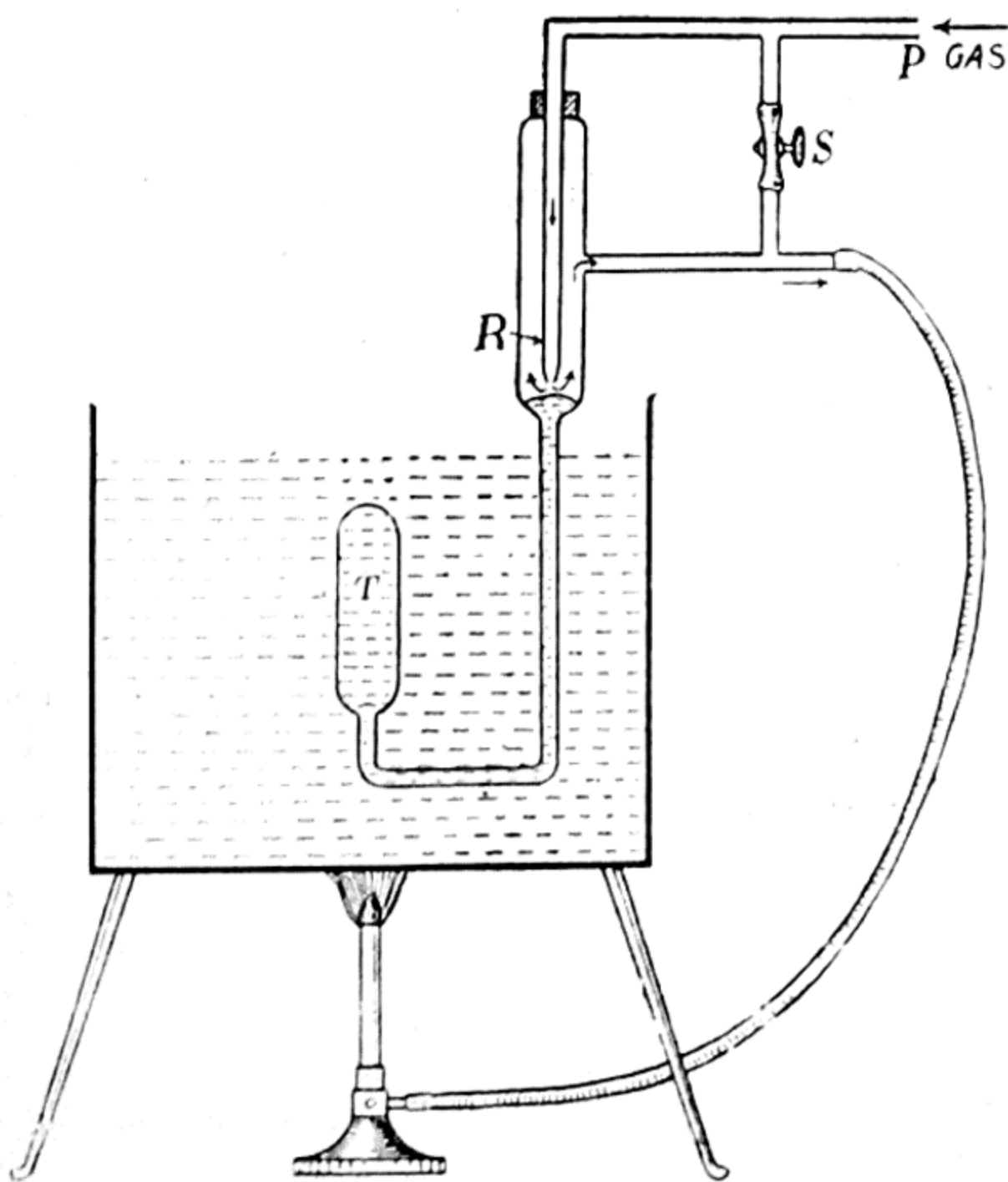


Fig. 2.8
Liquid Thermostat

(2) *Bi-metallic Thermostat* :—The heating in this case is electrical. When the temperature rises to the requisite value, an electric circuit

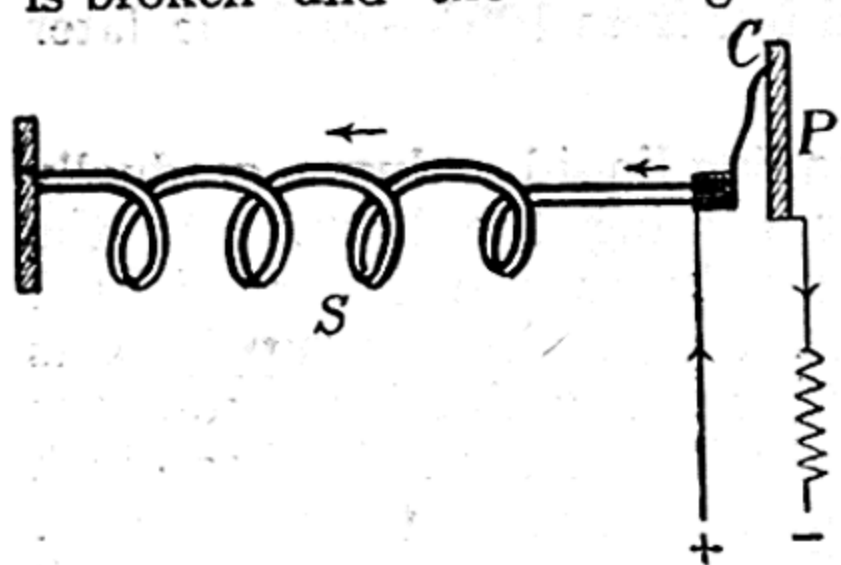


Fig. 2.9.
Bi-metallic thermostat

is broken and the heating stops but when the temperature falls slightly the contact is again established. S is a spring made of two metals with the more expansible metal on the outside. With a rise of temperature, the spring *curls inwards* more and more and it is so adjusted that when the requisite temperature has been reached, the metal contact C come off the plate P and the current is cut off. With a fall in temperature the spring unwinds itself and restores the connection.

QUESTIONS

1. What difficulties are encountered in measuring the expansion of crystals? How have they been overcome by Fizeau? Explain, in detail, his method for the above.

2. Show that cubical expansion is thrice the linear expansion for any substance. Give a method for measuring the real expansion of mercury and discuss the merits and demerits of the method you select.

3. Establish the Ideal Gas equation and evaluate the Gas constant. Is it a universal constant?

4. Explain the method of Comparator for determining the linear expansion of a solid. What is the chief merit of the arrangement.

5. Explain, in detail, the optical lever method of determining linear expansion of solids and work out the formula you would use.

6. What do you understand by the two coefficients of expansion of a liquid. How are they related to each other.

How will you determine experimentally the coefficient of apparent expansion of glycerine.

7. Discuss the influence of temperature on the density of liquids.

Explain Dulong and Petits method for determining the real expansion of mercury. Point out the weak points in their determination.

8. Describe one of Regnault's arrangements for determining the expansion of mercury and point out the merits of the method you select.

9. What do you mean by an ideal gas. Deduce the ideal gas equation and show that for an Ideal gas Volume Coefficient (α) = Pressure Coefficient (β).

10. What is the function of a Thermostat. How will you maintain a temperature of (i) 60°C and (ii) 200°C within a closed space.

11. A piston of radius 5 cm. moves in a cylinder made of a less expansible metal. What clearance must be allowed all round the piston at 50°C so that it may not get jammed at 250°C .

Coef. of expansion of piston = $0.00003/^\circ\text{C}$.

Coef. of expansion of cylinder = $0.00002/^\circ\text{C}$.

[Let the clearance be x cm. at 50°C . The radius of the cylinder at 50°C is $(5+x)$.

The radius of the piston at 250°C is

$$5[1 + 0.00003(250 - 50)]$$

....(i)

The radius of the cylinder at 250°C is

$$(5+x)[1 + 0.00002(250 - 50)]$$

.. (ii)

Equating (i) and (ii), we get

$$x = 0.01 \text{ cm. approx.}]$$

12. A clock which keeps correct time at 20°C has a pendulum made of iron (coef. of expansion $=0.00001$). How many seconds a day will it gain or lose when the temperature rises to 50°C ?

[Using the formula $T=2\pi\sqrt{\frac{l}{g}}$

$$T_1=2\pi\sqrt{\frac{l_{20}}{g}}=2 \quad \therefore \text{it keep correct time at } 20^{\circ}\text{C.}$$

$$\text{Also } T_2=2\pi\sqrt{\frac{l_{50}}{g}}$$

$$\therefore \frac{T_2}{T_1} = \sqrt{\frac{l_{50}}{l_{20}}} = \sqrt{\frac{l_{20}(1+30\alpha)}{l_{20}}} = 1+15\alpha$$

$$\text{or } T_2=2(1+15\alpha) \\ =2+30\times 0.00001$$

or in 2 seconds the clock loses 0.0003 Sec.

$$\therefore \text{ in 1 day the clock will lose } \frac{86400 \times 0.0003}{2} \text{ Sec.} \\ =12.96 \text{ Seconds.}]$$

13. A mercury barometer has a brass scale which is correct at 0°C . The barometer reads 29.5 inches at 20°C . Calculate the correct barometric height. Given α for brass $=0.000018$ and γ for mercury 0.00018 .

[If the apparent reading of the scale, whose graduations are correct at 0°C is h_1 at $t^{\circ}\text{C}$, then the actual length ht at $t^{\circ}\text{C}$ is $h_1(1+\alpha t)$.

$$\text{The actual pressure } =ht. \quad p_t \cdot g = h_1(1+\alpha t) \frac{p_0}{1+\gamma t} \cdot g \\ =h_1(1+\alpha t)(1-\gamma t)g p_0 \\ =h_1[1-(\gamma-\alpha)t]p_0g$$

and correct barometric height

$$h_0=h_1[1-(\gamma-\alpha)t] \\ =29.5[1-(0.00018-0.000018)20] \\ =29.403 \text{ inches.}]$$

14. A litre of hydrogen weighs 0.09 gm. at N.T.P. Calculate the weight of a litre of hydrogen at 27°C temperature and under 38 cm. pressure.

$$[\text{Using the relation } \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}]$$

$$\frac{38 \times 1000}{273+27} = \frac{76 \times V_2}{273}$$

$$\therefore \text{ the Volume of a litre of hydrogen under the later set of conditions} \\ = \frac{38 \times 1000}{300} \times \frac{273}{76}$$

$$=455 \text{ c.c. at N.T.P}$$

Now 1000 c.c. of hydrogen weigh 0.09 gm.

$$\therefore 455 \text{ c.c. } \quad \text{,,} \quad \text{will weigh } \frac{0.09 \times 455}{1000} \text{ gm.}$$

$$=0.041 \text{ gm.}]$$

CHAPTER III

CALORIMETRY

When you can measure what you are speaking about and express it in numbers, you know something about it, but when you cannot measure it, when you cannot express it in numbers your knowledge is of a meagre and unsatisfactory kind.—Lord Kelvin.

Historical. Thermometric scales, giving precision to the idea of temperature were developed, as stated already, early during the 18th century. The problem of *heat as a quantity* was not yet understood. People here and there had a vague idea that quantity of heat was somewhat dependent upon the mass of hot and cold bodies. Renadini and others showed that when unequal quantities of the *same* substance at different temperatures are mixed together, the rise or fall of temperature is very nearly proportional to the masses involved and to the difference in temperature, but the rule failed if the substances were unlike. Richman, in 1753, noticed that different substances cool at different rates but he had no clear ideas about temperature and thermal capacity and failed to draw any conclusions from his observations.

Heat was considered to be a material substance whose entry would increase the weight of the body. Boerhaave, however, got a negative result on weighing the same body cold and hot and was forced to the conclusion that *heat had no weight*, but the view was not accepted. The experiments of Lambert, Crawford and others developed the idea of specific heats, but the measurement of quantities of heat came in later (1760) after 'Change of State' had been understood. Joseph Black, in opposition to contemporary opinion, maintained, that large quantities of heat are necessary to bring about a change of state, even though there is no accompanying temperature rise. He thought melting to be a sort of a chemical reaction. He laid the foundation of calorimetry by his work with the ice-calorimeter and for the first time the question 'How much?' was answered. The discovery that made physicists discard the concept of heat as a material substance finally was that *heat is not conserved, but disappears when mechanical work is done e. g. by an expanding gas, which cools down in the process.*

3.1. Calorimetry.

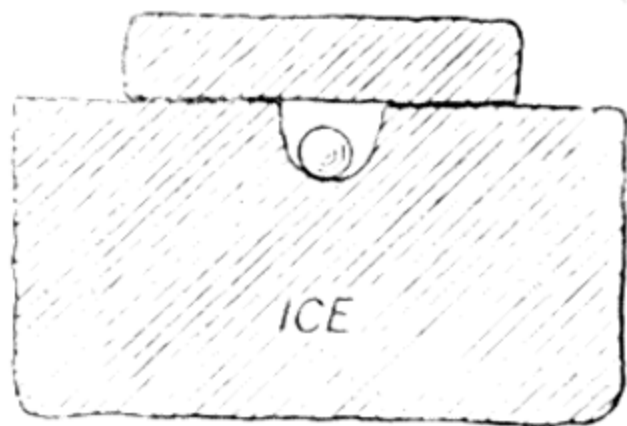


Fig. 3.1
Ice Calorimeter.

It means the science of measuring quantities of heat. That heat is a measurable quantity was first shown by Joseph Black. He scooped out a hollow in a block of ice, dried it with blotting paper, dropped into it two balls of copper of masses 100 gm. and 200 gm. respectively which had been heated in boiling water, one after the other. The hole was covered over with another block of ice. This arrangement he called an *ice calorimeter*. The mass of water formed by the

melting of ice (which he determined by soaking it into a piece of blotting paper) was double in the second case showing that

(i) Quantity of heat, Q , in a body \propto mass, m , of the body.

Next he took two balls of copper of equal mass but heated one to 50° and the other to 100° and dropped then one by one into his ice calorimeter. The water formed was double in the second case ; showing that

(ii) Quantity of heat in a body \propto its temperature, θ .

Next he heated two balls of equal mass but one made of copper and the other of iron, to the same temperature and introducing them into his calorimeter by turns, found that the amount of water formed was different in the two cases, showing that

(iii) Quantity of heat in a body depends on the nature, S , of its material. Combining we get

$$Q = m.S.\theta.$$

which is the fundamental law of calorimetry. S is known as *specific heat* of the material and is essentially the amount of heat necessary to raise the temperature of 1 gm. of the substance through 1°C .

It is also defined as the ratio of the quantity of heat required to heat up a certain mass of the substance through a given range of temperature to the heat required to heat up the same mass of water through the same range of temperature. Defined in this way, S is a number.

Heat is measured in calories. A *calorie* is defined as the amount of heat required to raise the temperature of one gram of water through 1°C . But the difficulty with this definition is that the temperature range is left undefined. We know that a gram of water will require different amounts of heat to raise its temperature, say, from 10° to 11° and from 60° to 61° . The temperature range usually selected is from 14.5°C to 15.5°C . It is known as the *15° Calorie* and is the amount of heat required to raise the temperature of 1 gram of water from 14.5°C to 15.5°C .

The *mean centigrade calorie* is one-hundredth part of the quantity of heat required to raise the temperature of one gram of water from 0°C to 100°C . It is about 0.02% greater than the 15° calorie.

3.2. Determination of Sp. heats. Method of Mixtures. The measurements are usually carried out in padded copper vessels called *calorimeters*. To determine the Sp. heat of a solid, small pieces of it are put in a copper tube which is heated in steam for some considerable time. The contents of the tube are then quickly dropped into a calorimeter containing a known weight of water at a known temperature. The mixture is well-stirred and the final temperature noted.

Let M be the mass of water, t_1 its initial temperature, t the final temperature and w the water-equivalent of the calorimeter (=mass of calorimeter \times Sp. heat of its material) and m the mass of solid and t_2 its temperature and S its sp. heat,

Heat lost by solid = $M.S.(t_2 - t)$ calories

Heat gained by calorimeter and water = $M.1.(t - t_1) + w(t - t_1).$

S can be determined by equating the heat lost to the heat gained.

Conversely, if the Sp. heat of a solid is known that of a liquid can be determined by substituting it for water in the calorimeter.

It will be noticed that as soon as the liquid begins to gain heat, it becomes hotter than its surroundings and therefore begins to lose heat to them by radiation. As a consequence the final temperature is a bit too low. A simple method of allowing for the radiation loss is the following :—

The calorimeter and its contents are allowed to cool for an interval of time equal to that taken by the experiment. Half the fall of temperature observed, is added to the final temperature. This can be justified as follows. Since the temperature of the calorimeter rises gradually from the room-temperature to its maximum value, the average excess of temperature can be taken to be equal to half the maximum excess ; hence cooling produced during the experiment is half the cooling at the final temperature.

3.3. Bunsen's Ice Calorimeter. The unique feature of this calorimeter is that the amount of ice melted is measured by noting the change of volume and not by weighing. It is based on the principle that when one gram of ice melts to water at 0°C , a contraction of 0.087 c.c. takes place in its volume.

A glass test tube *A* is fused into a wider tube *B* as shown.

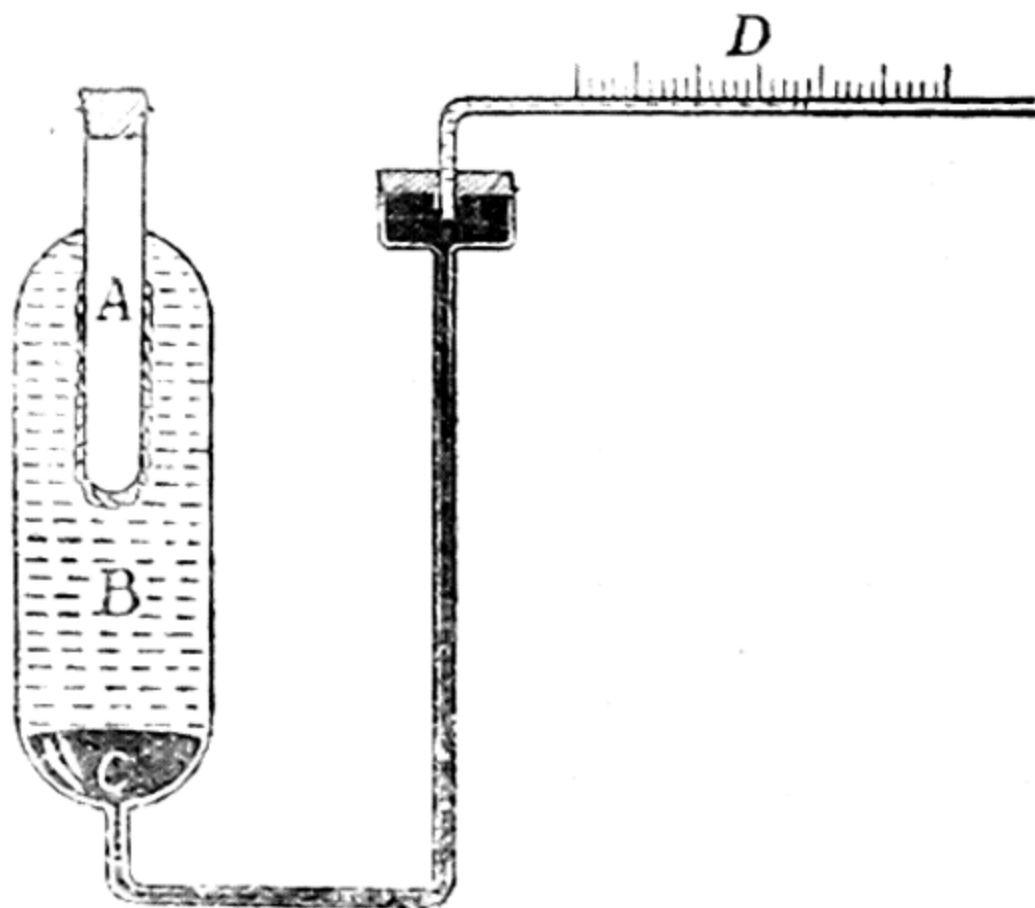


Fig. 3.2
Bunsen's Ice-Calorimeter.

The part *B* is filled with pure air-free water, *C* is mercury, while the capillary *D* contains coloured alcohol. The whole apparatus is put in pure ice at 0°C . A piece of solid CO_2 is dropped in *A* and is kept there till a little ice forms on the outside of *A*. The CO_2 is then removed and chilled alcohol is circulated through *A*, till a layer of ice, a millimeter or two thick, forms. The alcohol is also removed and the ice is allowed to warm up to 0°C i.e., to the temperature of the ice in which the apparatus is now embedded.

A small quantity, *m*, of the experimental substance is heated to a known temperature *T* and dropped into *A*, which holds some water

to absorb the shock and to transmit the heat given out by the substance to the ice outside *A*. Some ice melts and the column of coloured alcohol recedes in the capillary. If *v* is the contraction in volume, the mass of ice melted is $v/0.087$, and if *L* be the latent heat of ice, the heat absorbed is $L.v/0.087$ calories. The heat given out by the solid in cooling to 0°C is $m.T.S$.

Now
$$m.T.S. = Lv/0.087$$

or
$$S = (Lv/0.087) \times \frac{1}{mT}$$

The instrument can measure very small quantities of heat and can, therefore, be used to determine the Sp. heat of very small specimens. It has other advantages :—

- (i) There is no loss or gain of heat to or from outside.
- (ii) The stirrer, thermometer etc., are not needed.

Sp. heats of some common substances at ordinary temperatures :—

Substance	Sp. heat	Substance	Sp. heat
Aluminium	0.21	Brass	0.088
Diamond	0.122	Glycerine	0.58
Copper	0.091	Turpentine	0.42
Iron	0.105	Paraffin wax	0.69
Lead	0.03	Sand	0.19
Mercury	0.033	Glass (crown)	0.16
Zinc	0.092	Sea-water	0.94

3.4. Metal block calorimeter. In the method of mixtures for determining specific heats, water is used as the calorimetric substance. But water has its limitations. If a body at a high temperature be dropped into the calorimeter, steam or vapours may be evolved and will escape, producing errors. Such errors are eliminated in the Nernst Calorimeter.

A block of copper, *B*, fits into a Dewar flask and another copper block *C* is used to close the mouth of the flask. One junction of each of the thermo-couples T_1 and T_2 is inserted in block *B* and is in good thermal contact with it, while the other junctions are embedded in the block *C* which is maintained at a constant temperature by immersing the flask in a bath. The heated substance is dropped into the flask through a glass tube *D* which is secured in *C* and the tube is immediately closed with a plug of cotton to prevent loss of heat through it. The heated body loses heat to the block *B*, and this heat quickly spreads all over the block (copper being a very good conductor). The body and block come to a common temperature which is given by the thermo-couples. If the water-equivalent of *B* is known, specific heat can be easily calculated.

This calorimeter possesses many advantages.

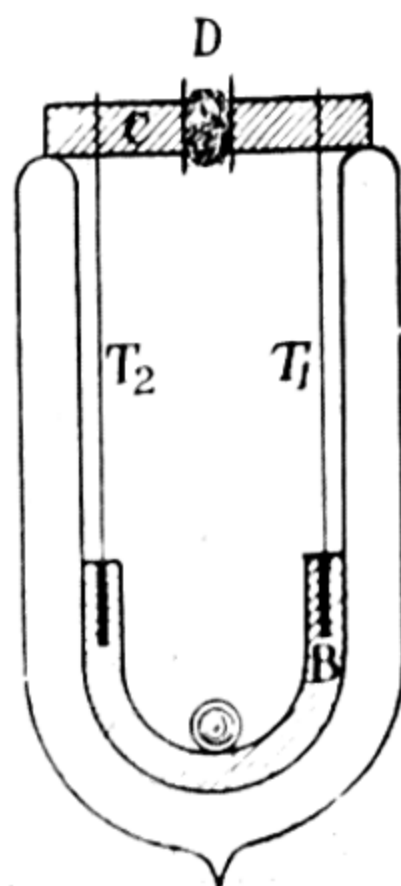


Fig. 3.3 Block Calorimeter

1. The loss of heat across the Dewar flask is negligible and no radiation correction is needed.

2. The thermal capacity of copper being much less than that of water, the rise of temperature is larger.

3. Copper being an excellent conductor, final temperature is quickly attained.

4. It is an excellent method for determining specific heats at high temperatures.

3.5. Vacuum Calorimeter. To determine the specific heat of metals at low temperatures, a block of the metal consisting of two parts *A* and *B* fitting tightly into each other at the top while leaving a small annular space at the bottom, is used. Insulated platinum wire is wrapped round *A*. The cylinder is suspended in a vessel and cooled to the desired temperature (if necessary in liquid air). The vessel is then exhausted and sealed. This serves to cut off heat losses.

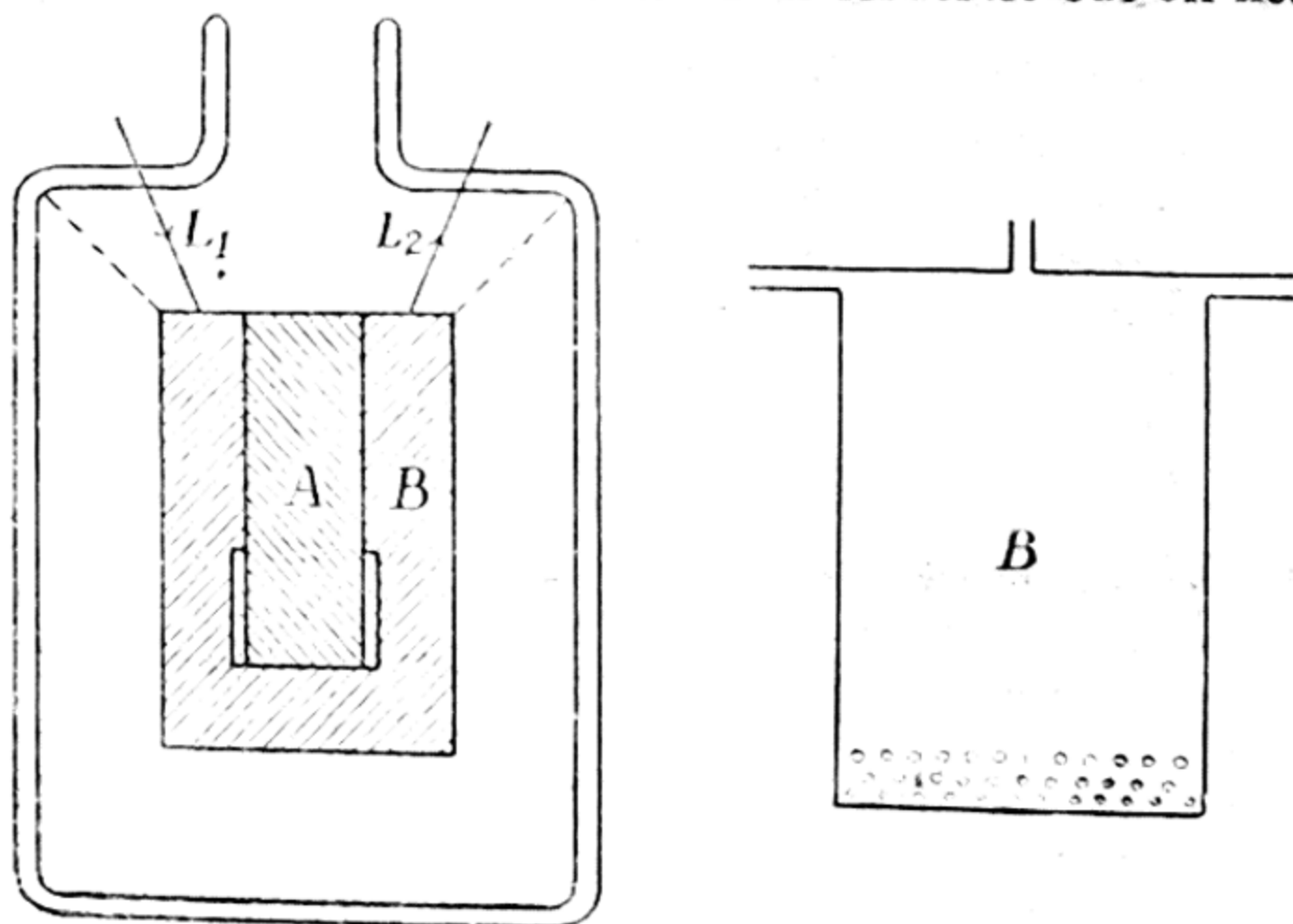


Fig. 3.4
Vacuum Calorimeter.

A current of known amperage and at a known voltage is sent round the platinum wire through the leads L_1, L_2 . The temperature rise (usually about 1°C) is measured by the change in the resistance of the platinum wire which thus serves the double purpose of a heating element and a platinum thermometer.

The heat produced electrically is $\frac{E \cdot I \cdot t}{4.2} = M \cdot S \cdot \theta$. where E = potential difference in volts ; I , the current in amperes ; t the time in seconds ; M the mass of AB ; θ , the rise of temperature and S the required specific heat.

If the substance is a non-metal or a bad conductor, a slight variation of the above method is used. B is now a thin silver vessel, in which the substance (cut into small pieces) is put. Heating is done by wrapping a resistance wire round B on the outside. A gas,

usually hydrogen, is contained in B . A lid is now sealed on B . B is then suspended as above. The gas is used to establish a thermal equilibrium inside the silver vessel.

3.6. A Note on Logarithms.

(1) If

$$a^x = N$$

Then

$$x = \log_a N.$$

Thus

$$10^3 = 1000$$

\therefore

$$3 = \log_{10} 1000$$

Logarithms to the base 10 are called *common* logarithms

(2)

$$\begin{aligned} \log_b N &= \frac{1}{\log_a b} \times \log_a N \\ &= \log_b a \times \log_a N \end{aligned}$$

In particular,

$$\begin{aligned} \log_e N &= \frac{1}{\log_{10} e} \times \log_{10} N \\ &= \log_e 10 \times \log_{10} N = 2.3 \log_{10} N \end{aligned}$$

$$e = 2.718 \dots$$

Logarithms to the base e are called *Natural* logarithms and are denoted by l_n .

\therefore

$$l_n N = 2.3 \log_{10} N \quad \dots (a)$$

or

$$\log_{10} N = 0.43 l_n N \quad \dots (b)$$

Relations (a) and (b) are important.

$$(3) \quad \log_a M + \log_a N = \log_a MN$$

$$\log_a M - \log_a N = \log_a \frac{M}{N}$$

$$N \log_a M = \log_a M^N$$

$$a^x = e^{x \log_a a}$$

$$(4) \quad \log_e(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots \quad (x < 1)$$

$$\log_e(1-x) = -x - \frac{x^2}{2} - \frac{x^3}{3} - \frac{x^4}{4} - \dots \quad (x < 1)$$

NOTE.—In all theoretical deductions logarithms are always referred to the base e . To convert them to common logarithms always divide them by 2.3.

3.7. A note on Differentiation.

(1) Consider the equation,

$$y = x^2$$

$\dots (i)$

Any change in the value of x produces a corresponding change in y . Here x is the *independent variable* and y the *dependent variable*.

Suppose x gets a slight increase Δx . This will also produce a slight increase Δy in the value of y . Hence.

$$\begin{aligned} y + \Delta y &= (x + \Delta x)^2 \\ &= x^2 + 2x \cdot \Delta x + \Delta x^2 \end{aligned}$$

$\dots (ii)$

Subtract (i) from (ii)

$$\therefore \Delta y = (x^2 + 2x \cdot \Delta x + \Delta x^2) - x^2 \\ = 2x \cdot \Delta x + \Delta x^2$$

$$\text{Now } \frac{\Delta y}{\Delta x} = \frac{2x \cdot \Delta x + \Delta x^2}{\Delta x} = 2x + \Delta x$$

If now Δx tends to zero, Δy also tends to zero but the ratio $\frac{\Delta y}{\Delta x}$ is generally finite.

$$\lim_{\Delta x \rightarrow 0} \frac{\Delta y}{\Delta x} = \frac{dy}{dx} = 2x + 0 \\ = 2x$$

$\frac{dy}{dx}$ is called the *differential co-efficient* of y with respect to x . It measures the ratio of the change in y produced by a slight change in the value of x to the change in x , when the increment in x is infinitesimal. If the curve $y = x^2$ be plotted, $\frac{dy}{dx}$ gives the slope of the curve i.e., the inclination of the tangent to the curve at the point considered.

Similarly, if

$$y = x^3 \\ \frac{dy}{dx} = 3x^2$$

and if

$$y = \frac{1}{x} = x^{-1} \\ \frac{dy}{dx} = -1 \cdot x^{-1-1} = -\frac{1}{x^2}$$

Generally, if $y = x^n$, when n is +ve or -ve, integral or fractional

$$\frac{dy}{dx} = n \cdot x^{n-1}$$

The differential co-efficient of $\frac{dy}{dx}$ i.e. $\frac{d}{dx} \left(\frac{dy}{dx} \right)$ is called the second differential co-efficient of y with respect to x and is written $\frac{d^2y}{dx^2}$.

Hence if

$$y = x^n \\ \frac{dy}{dx} = n \cdot x^{n-1} \\ \frac{d^2y}{dx^2} = n(n-1)x^{n-2}$$

(2) Differential coef. of $\log_e x$ with respect to x i.e. $\frac{d}{dx} (\log_e x) = \frac{1}{x}$.

(3)

$$\frac{d}{dx}(y.z) = \frac{dy}{dx} \cdot z + y \cdot \frac{dz}{dx}$$

$$\frac{d}{dx}\left(\frac{y}{z}\right) = \frac{\frac{dz}{dx} y - z \cdot \frac{dy}{dx}}{z^2}$$

(4)

$$\frac{dy}{dx} = \frac{dy}{dz} \cdot \frac{dz}{dx}$$

(5) Diff. coef. of a constant is zero.

(6) If $pv = \text{constant}$. $p \cdot dv + v \cdot dp = 0$.

Here the independent variable is not specified. dp and dv are called *differentials*.

If $pv^\gamma = \text{constant}$, where γ is a number

$$p\gamma v^{\gamma-1} dv + v^\gamma dp = 0.$$

3.8. A note on Integration. (1) Integration may be considered an inverse process to differentiation. Thus the differential coefficient of x^2 is $2x$, hence the integral of $2x$ is x^2 and that of x is $\frac{x^2}{2}$. This is written as

$$\int x \cdot dx = \frac{x^2}{2}$$

dx denoting that x is the variable.

$$(2) \quad \int x^n dx = \frac{x^{n+1}}{n+1}.$$

$$(3) \quad \int \frac{1}{x} \cdot dx = \log x.$$

$$\int \frac{dp}{p} = \log p.$$

(4) Consider the integral

$$\int_a^b y \cdot dx.$$

... (a)

when y is a function of x .

If we plot the curve $y=f(x)$, (say $y=x^2$), the integral (a) gives the area ABCD included between the curve, the x -axis and the ordinates $x=a$ and $x=b$, a and b are called the limits of the integral. Such integrals are called *definite integrals*.

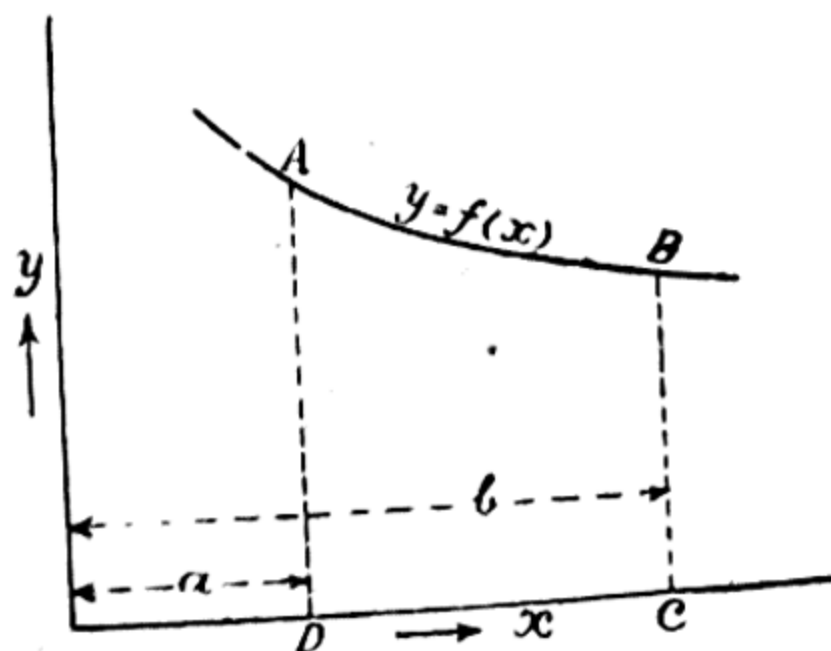


Fig. 3.5.

Area defined by an integral

3.9. Newton's Law of Cooling. A hot body when left to itself gradually cools down to the temperature of its surroundings. Newton found that the rate at which a hot body cools, i.e., the number of calories of heat lost by it per second depends on the difference of

depends on the difference of

temperature between the hot body and its surroundings. This is known as the *Newton's law of cooling*. One of the conditions laid down is that the hot body should be exposed to draughts, *i.e.*, it should either be placed facing an open window or under a fan. Under these circumstances, the law is true for quite large temperature-differences. If, however, the hot body be protected from draughts, the rate of loss of heat is proportional to the $\frac{5}{4}$ th power of the temperature difference.

The rate of loss of heat also depends upon.

(1) The *area* of the exposed surface—the larger the area, the more rapid the cooling.

(2) The *nature* of the exposed surface—cooling being more rapid for dull black surfaces and slower for polished ones.

The law of cooling appears to make sense only in the case of liquids, because the temperature of cooling liquids is equalized throughout their mass either by convection currents or can be equalized by stirring. In the case of heated solids, the temperature increases from the surface inwards and the phrase 'difference of temperature between the hot body and surroundings' has no meaning because the solid does not possess *one* temperature. The rate of flow of heat from the interior of a solid towards surface depends on the heat conductivity of the solid.

Consider a hot body of mass m , sp. heat s and temperature θ . Let θ_0 be the temperature of its surroundings. If the temperature falls by $\delta\theta$ in a time δt , the heat, δH , lost by the body in the interval δt is

$$-\delta H = m.s. (-\delta\theta)$$

and the heat lost per second is

$$-\frac{\delta H}{\delta t} = -m.s. \frac{\delta\theta}{\delta t}$$

and in the limit

$$-\frac{dH}{dt} = -m.s. \frac{d\theta}{dt} \quad \dots(i)$$

Also by Newton's law of cooling

$$-\frac{dH}{dt} = K(\theta - \theta_0), \quad \dots(ii)$$

K being a constant depending on the nature and area of the cooling surface.

Combining (ii) with (i)

$$-ms. \frac{d\theta}{dt} = K(\theta - \theta_0)$$

or

$$-\frac{d\theta}{dt} = K'(\theta - \theta_0) \quad \dots(iii)$$

where

$$K' = K/ms.$$

This is an important relation. It can be put in the alternative form

$$\frac{d\theta}{\theta - \theta_0} = -K' . dt \quad \dots(iv)$$

Integrating (iv)

$$\int \frac{d\theta}{\theta - \theta_0} = -K' \int dt$$

$$\log(\theta - \theta_0) = -K't + C \quad (v)$$

or

where C is the constant of integration .

Example 1. If a body takes 3 minutes to cool from 100° to 60°C , how many minutes will it take to cool from 60° to 20°C . Assume that the temperature of the surroundings is 10°C and that Newton's law of cooling is obeyed throughout.

$$\theta_0 = 10^\circ$$

$$t = 3 \text{ minutes}$$

Now,
$$\int_{60}^{100} \frac{d\theta}{\theta - \theta_0} = -K' \int_0^3 dt$$

$$\therefore \left[\log(\theta - \theta_0) \right]_{60}^{100} = -K' \left[t \right]_0^3$$

$$\log_e 90 - \log_e 50 = -K' . 3 \quad (i)$$

or

Similarly
$$\int_{20}^{60} \frac{d\theta}{\theta - \theta_0} = -K' \int_0^t dt$$

$$\log_e 50 - \log_e 10 = -K' t \quad (ii)$$

or

dividing (ii) by (i)

$$\frac{\log_e 50 - \log_e 10}{\log_e 90 - \log_e 50} = \frac{t}{3} .$$

or

$$\frac{2.3[\log_{10} 50 - \log_{10} 10]}{2.3[\log_{10} 90 - \log_{10} 50]} = \frac{t}{3} .$$

$$\frac{1.69897 - 1}{1.95424 - 1.69897} = \frac{t}{3} .$$

or

$$t = 8.22 \text{ minutes.}$$

Example 2. If a body cools in 3 minutes from 100° to 60°C , how much will the body cool in the next 3 minutes, assuming Newton's law of cooling to hold throughout. The temperature of the surroundings is 10°C .

Let θ' be the final temperature after a further 3 minutes.

$$\int_{60}^{100} \frac{d\theta}{\theta - 10} = -K' . 3$$

\therefore

$$\log_e 90 - \log_e 50 = -K' . 3 \quad \dots(i)$$

Also

$$\int_{\theta'}^{60} \frac{d\theta}{\theta - 10} = -K' . 3$$

$$\begin{aligned}
 \text{or} \quad & \log_e 50 - \log_e (\theta' - 10) = -K' \cdot 3 \\
 \therefore & \log_e 90 - \log_e 50 = \log_e 50 - \log_e (\theta' - 10) \\
 \text{or} \quad & 2 \cdot 3 [\log_{10} 90 - \log_{10} 50] = 2 \cdot 3 [\log_{10} 50 - \log_{10} (\theta' - 10)] \\
 \text{or} \quad & \log_{10} (\theta' - 10) = 2 \log_{10} 50 - \log_{10} 90 \\
 & = 1 \cdot 44370 \\
 \therefore & \theta' - 10 = 27 \cdot 8 \\
 \text{or} \quad & \theta' = 37 \cdot 8^\circ \text{C}
 \end{aligned}$$

3.10. Sp. Heat by Law of Cooling. The rate of cooling of a hot body depends upon the difference of temperature between the hot body and surroundings and on the nature and extent of the *exposed* surface. It follows therefore that the rate of loss of heat does *not* depend on the nature of the contents of a vessel. In

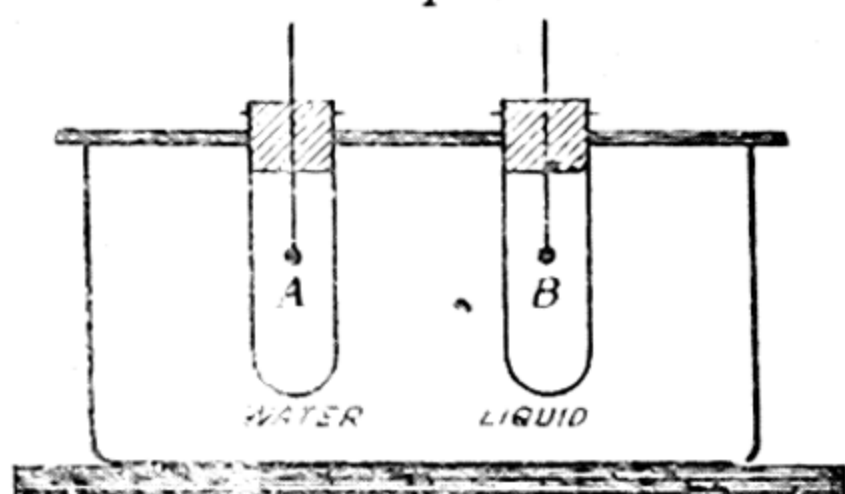


Fig. 3.6

Law of cooling apparatus

other words, *under similar conditions, all bodies will cool at the same rate.* This is the basis of a method for determining the sp. heat of a liquid.

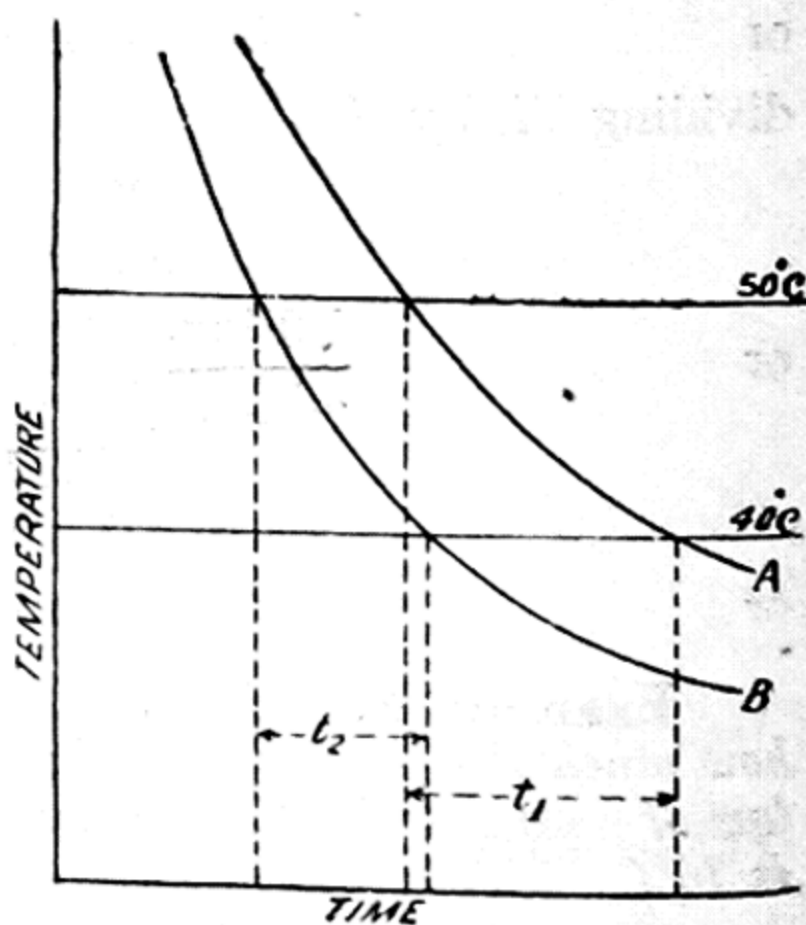
Two identical calorimeters A and B containing *equal volumes* of water and of the experimental liquid respectively, are heated to about 70°C and then suspended in a large vessel as shown.

The temperature of both calorimeters is noted separately every minute and a cooling curve drawn for each. The times t_1 and t_2 taken by the water and the liquid to cool from, say 50° to 40°C are determined from the graph. Then if m_1 and m_2 be the masses of water and liquid, w_1 and w_2 the water-equivalents of calorimeters, and s the sp. heat of the liquid, heats lost per second by the two being equal

$$\frac{(m_1 + w_1)10}{t_1} = \frac{(m_2 s + w_2)10}{t_2}$$

from which s can be easily calculated.

The method is not very accurate. It is only used to determine approximately the sp. heats at inconvenient temperatures, where no other method is practicable.

Fig. 3.7
Cooling curves.

Example 3. The times taken by 50 c.c. of water and 50 c.c. of a liquid of sp. gravity 0.8, to cool from 55° to 45°C are respectively 60 sec. and 40 sec. If the water-equivalent of each calorimeter be 5 gm., determine the sp. heat of the liquid.

Mass of water, m_1	$=50 \times 1 = 50$ gm.
Mass of liquid, m_2	$=50 \times .8 = 40$ gm.
Fall of temperature	$=55^\circ - 45^\circ = 10^\circ\text{C}$
Time taken by water, t_1	$=60$ seconds.
Time taken by liquid, t_2	$=40$ seconds
Water-equivalent, w	$=5$ gms.

Let s be the sp. heat of the liquid, then

$$\frac{(50+5)10}{60} = \frac{(40s+5)10}{40}$$

or

$$s = .79.$$

3.11. Two Specific Heats of a Gas. Specific heat is essentially the amount of heat required to raise the temperature of a unit mass of a substance through 1°C . A gas can, however, be heated by a mere compression without supplying any heat to it. Its specific heat,

$S = \frac{Q}{1.\theta}$, in that case is zero. Again, suppose that while a gas is

being heated, it is also allowed to expand against the external pressure at such a rate that the cooling due to expansion *just* cancels the heating. Here, although heat is flowing into the gas, there is 0°

rise of temperature and $S = \frac{Q}{\theta}$ is ∞ . Hence, a gas can have any specific heat between 0 and ∞ depending upon conditions under which the heating takes place. Two specific heats are, however, important:—

- (i) C_v or specific heat at constant volume, and
- (ii) C_p or specific heat at constant pressure.

In fig. (i) one gram of a gas having a volume V is sealed in an air-tight box. When heat is supplied, no increase of volume can take place. All the heat supplied is used up only in raising its temperature.

In fig. (ii) the box in which the gas is enclosed has a movable lid. When heat is supplied to the gas, its pressure increases and moves the lid upwards against the external atmospheric pressure, p and this outward movement continues till the pressures inside and outside have been equalized. If the increase in volume is dv , the external work done by the gas is $p.dv$ and to do this work, the gas will draw an additional amount of heat.

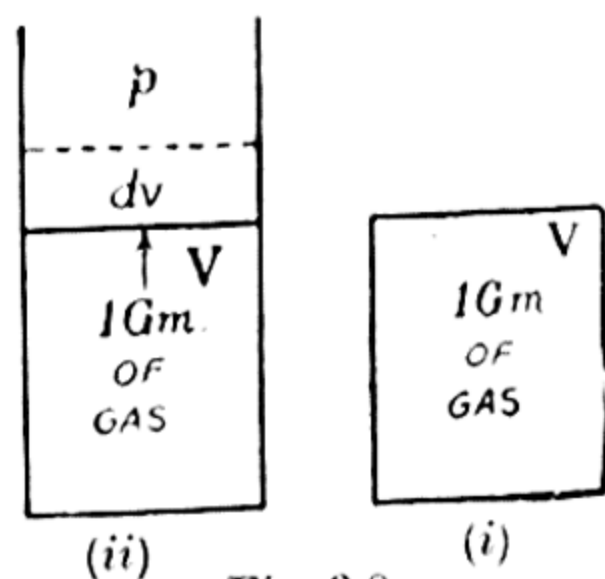


Fig. 3.8
To Illustrate C_p and C_v .

Heat, in this case, is used up.

- (a) to raise the temperature of the gas through 1°C as in the first case, and
- (b) to do work, $p.dv$, against external pressure,

Hence $C_p > C_v$ by an amount equal to the thermal equivalent of the external work done by the gas.

3.12. Determination of C_v . Jolly's Method.

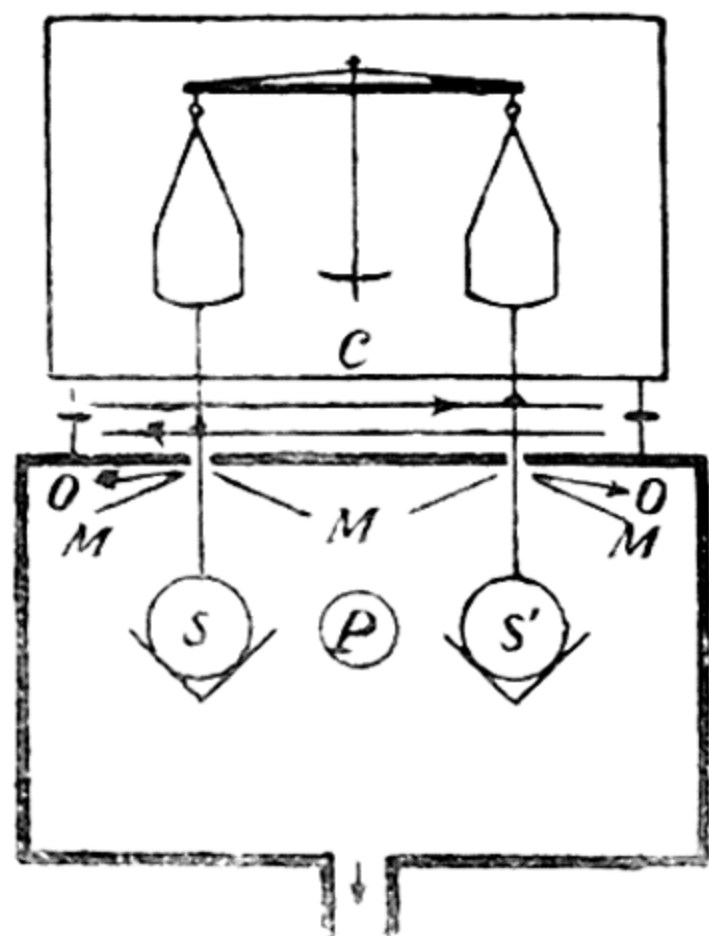


Fig. 3.9

Jolly's apparatus for C_v .

Two identical copper spheres are suspended in a thick-walled wooden chamber with the help of thin wires attached to a sensitive balance placed on the chamber. The spheres are exhausted of all air and counterpoised. S is now filled with the experimental gas and the weight W of the gas is determined. It is then allowed to attain the temperature t_1 of the enclosure, which is recorded with a sensitive thermometer. Steam is now admitted into the chamber through the inlet pipe P situated symmetrically between the two spheres. The temperature t_2 of the steam is carefully measured. More steam condenses on S than on S' and the water formed is collected in pans attached to the spheres. The extra amount m of the steam condensed on S is due to the heating of the

enclosed gas.

Any water tending to fall on the spheres from the ceiling of the chamber is drained off by thin metal shields MM . In order that any drops of water condensed in the holes OO may not interfere with the free swing of the suspending wires, the holes are lined with plaster of Paris and the wires themselves are kept hot with an electric current flowing through the wire C wrapped loosely round the suspending wires.

If L is the latent heat of steam, the heat lost by it is $m.L$ calories and that gained by the gas $W.C_v.(t_2 - t_1)$ calories.

Hence

$$mL = W.C_v.(t_2 - t_1)$$

whence, C_v is calculated.

The spheres S and S' are now interchanged and the experiment is repeated with the gas in S' . The mean is the value of C_v .

Correction must be applied for the fact that (i) the spheres expand on heating and therefore a buoyancy correction must be applied to the weights at the higher temperature

(ii) Due to the expansion of the sphere, the gas also expands. Its volume does not remain constant. It absorbs a certain amount of heat in expanding to its new volume. If H be the heat taken up for this purpose

$$mL - H = W.C_v.(t_2 - t_1)$$

The weight m of the water condensed should also be reduced to vacuo for extreme accuracy.

3.13. Determination of C_p .—(a) Regnault's Method.

The experimental gas is stored in a stout steel holder H placed in a tank

of water. Tap P is opened and by turning the regulating screw V , a slow supply of gas at a constant pressure (as indicated by the manometer M) is led through the copper coil C immersed in an oil-bath which is heated from below. As the pressure of the gas in H falls, V is opened more and more so that the pressure of the gas entering C remains unaltered throughout. A long coil is used so that the gas may have sufficient time to acquire the temperature of the bath. This heated gas at a temperature t_1° is led into a calorimeter K of water-equivalent w_1 containing w_2 grams of water at t_2° . After

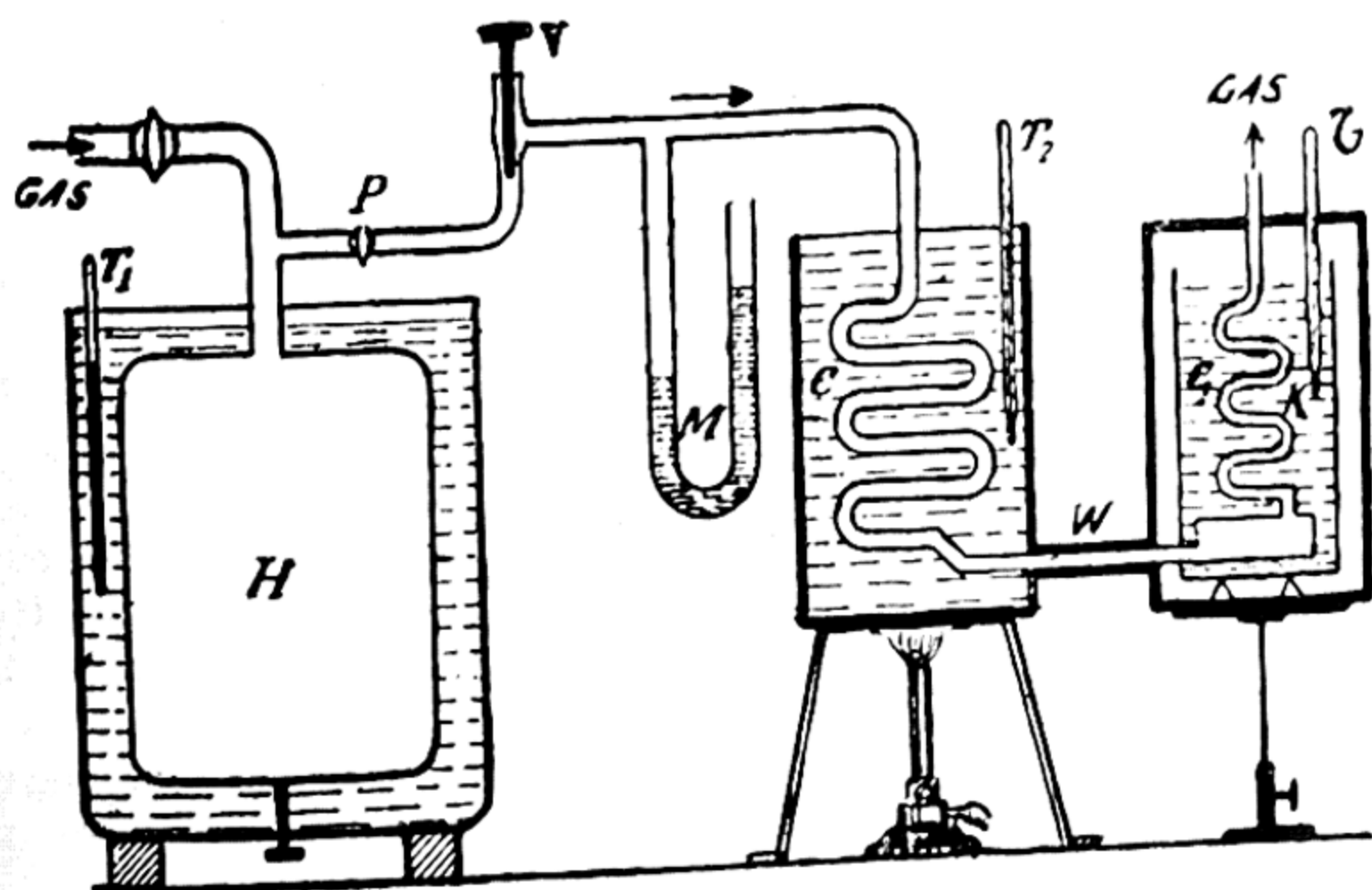


Fig. 3.10
Regnault's apparatus for C_p .

flowing through the coil C_1 of water-equivalent w_3 , the gas escapes into the air at a temperature t_3 —the final temperature of the calorimeter and its contents.

To prevent conduction of heat across the coil CC_1 , it is arranged that C terminates at the left of a stout wooden cylinder (which is a poor conductor) having a tubular hole across it. C_1 is joined to the right of it. To prevent the flow of heat by radiation, the oil-bath as well as the calorimeter have thick wooden coverings and the calorimeter is also well-padded.

Since the gas flows at a uniform rate, on the average it is cooled from t_1 to $\frac{t_2+t_3}{2}$. If m be the mass of the gas that flows through the calorimeter, the heat lost by the gas is

$$m.C_p. \left(t_1 - \frac{t_2+t_3}{2} \right)$$

and since the temperature of the calorimeter and its contents rises from t_2 to t_3 , heat gained by it is

$$(w_1 + w_2 + w_3)(t_3 - t_2)$$

$$\text{Hence } m.C_p. \left(t_1 - \frac{t_2 + t_3}{2} \right) = (w_1 + w_2 + w_3)(t_3 - t_2) \quad \dots(i)$$

whence C_p is calculated.

The mass m of the gas is determined indirectly by noting the gas-pressure of the holder at the beginning and at the end of the experiment. If the pressure falls from p_1 to p_2 and v is the volume of the holder and t its temperature, the volume of the gas that has flowed out of it, is given at N.T.P. by the relation

$$\frac{(p_1 - p_2)v}{273 + t} = \frac{76x}{273} \text{ or } x = v. \frac{p_1 - p_2}{76} \cdot \frac{273}{273 + t}$$

Since mass = density \times volume

$$m = \rho.x = \rho.v. \frac{p_1 - p_2}{76} \cdot \frac{273}{273 + t}$$

where ρ is the density of the gas at N.T.P.

There is an important source of error in the experiment. The calorimeter gains heat from the bath by radiation, along the pipe by conduction and from the wooden screen by convection, but it also loses heat to the surroundings by radiation. On the whole, however, it gains more heat in this way than it loses. Hence the final temperature t_3 is much too high. To apply the necessary correction, the experiment is divided into three parts :

(1) Without starting the flow of gas, the rise in the temperature of water, δt_1 is observed for ten minutes. Heat is brought to the calorimeter by agents other than the hot gas.

(2) The flow of gas is now established and the rise of temperature is observed for another 10 minutes.

(3) The gas-flow is now discontinued and the rise of temperature of water, δt_2 , is again observed for a further period of 10 minutes.

A quantity $\delta t = \frac{1}{2} (\delta t_1 + \delta t_2)$ is subtracted from the final temperature t_3 . The last factor in equation (i) is altered to $[t_3 - (t_2 + \delta t)]$.

3.14. A note on Electrical Quantities. (1) Three important quantities connected with direct current electric circuits are current-strength, resistance and potential difference. The rate of flow of charge across any cross-section of a conductor in the *current*; the opposition offered by a conductor to the passage of electricity across it, is its *resistance*; while *potential difference* is current \times resistance. These quantities are measured theoretically in *absolute* units, but these units are either too big or too small for practical purposes. The second type of units, adopted for practical needs are called *practical* units.

Quantity	Practical unit	Relation to absolute unit
Current	Ampere	10^{-1} times
Resistance	Ohm	10^9 times
Pot. difference	Volt	10^8 times

(2) $10^7 \text{ ergs} = 1 \text{ joule}$

$1 \text{ Joule or } 10^7 \text{ ergs per sec} = 1 \text{ watt}$

$4.2 \times 10^7 \text{ ergs} = 1 \text{ calorie}$

or $4.2 \text{ Joules} = 1 \text{ calorie}$

(3) $\text{amperes} \times \text{volts} = \text{watts}$

Joule is the unit of work and energy, while watt is the unit of power.

i.e., $\text{Joule} = \text{watt} \times \text{second}$

If a current of I amperes flows through a potential difference of E volts for one second, the energy spent is $E \times I$ joules. If all this energy be converted into heat, the heat developed is $E \times I / 4.2$ calories.

3.15. Determination of C_p —(b) Continuous Flow Method.
In this extremely accurate arrangement due to Scheel and Heuse, the

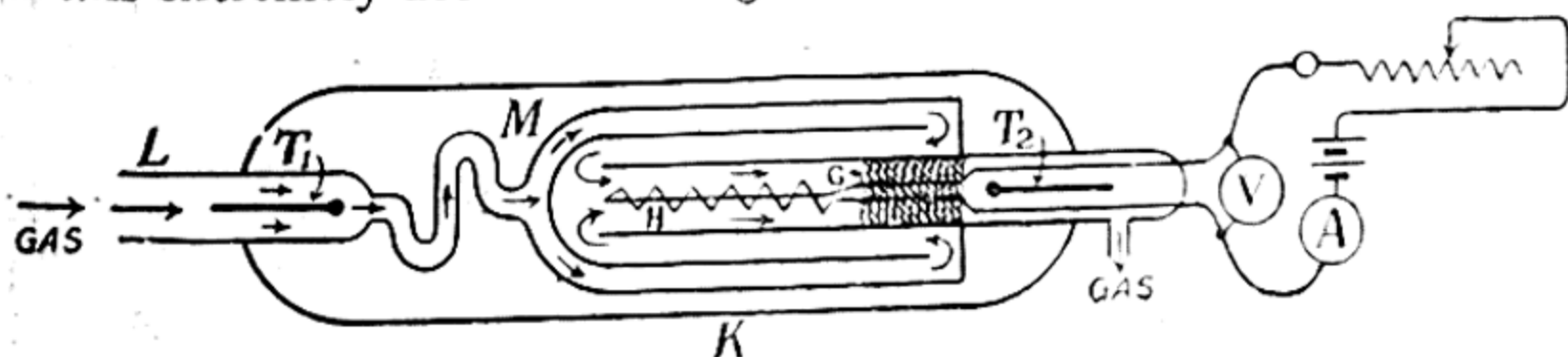


Fig. 3.11.
Continuous flow method for C_p .

the calorimeter K which is made of glass, is sealed in an exhausted tube M to reduce loss of heat. The apparatus is placed in a constant-temperature bath. After passing slowly through a long metal tube L which is immersed in the same bath, the gas flows past the platinum thermometer T_1 (which measures the initial temperature, t_1 , of the gas) into the calorimeter K . Travelling in the direction of the arrows, the gas comes in contact with the heating element H and after passing through the copper-gauze packing G , where it is thoroughly mixed, flows out to the right past the platinum thermometer T_2 . The advantage of this zig-zag arrangement is that any heat lost by the heated gas is brought back into it by the incoming stream and none is wasted. When the steady state has been reached, the final temperature t_2 of the gas is read by the thermometer T_2 .

If m is the mass of the gas that flows through the calorimeter per second, the heat gained by the gas is $m \cdot C_p \cdot (t_2 - t_1)$. This heat has been produced in the coil electrically. If I amperes be the current flowing through the coil H and E volts be the P. D. at its ends, the heat generated per second is $E I / 4.2$ calories.

Hence
$$m \cdot C_p \cdot (t_2 - t_1) = \frac{EI}{4.2}$$

whence C_p can be calculated.

This method possesses several distinct advantages.

(1) The radiation losses are negligible.

(2) Heat is produced electrically and can be measured with great exactness.

(3) Steady temperatures can be recorded with a greater precision than changing ones.

(4) The thermal capacity of the arrangement is automatically eliminated because when the steady state is reached, the temperatures at the various points of the apparatus become constant.

(5) Since heating can be controlled, the method can be used to examine if the sp. heat varies with temperature.

(6) The method is neater and much more compact than the Regnault's arrangement.

3.16. Bomb Calorimeter.

It is an arrangement for determining the calorific value of fuels and the heats of combustion of various substances *i.e.*, for finding how many calories of heat are liberated when one gm. of the substance under test is completely burnt.

It consists of a stout cylinder *A*, of steel, to which a strong steel lid can be screwed. The substance, if a solid, is dried, powdered and carefully weighed and then placed in the platinum crucible *C*, which is held in position within the bomb *A* by means of a loop of wire *RR*. If the substance under test is a liquid, it is soaked in pure cellulose and then put in the crucible. Oxygen, under a pressure of about 25 atmospheres and thrice in weight of the quantity just needed for complete combustion of the material is admitted into the bomb through the tube *B* by opening the cocks *GG*, which are then closed.

A piece *W* of thin platinum wire is placed in the crucible so that it is completely embedded in the substance. Copper leads *LL* are joined to the ends of *W* and pass out through the lid but are *insulated* from it. The bomb is then placed in a calorimeter *P* of known water equivalent containing a known weight of water. The temperature of the water is recorded with a sensitive thermometer *T*. The leads *LL* are now connected to a battery, a strong current from which heats up the platinum coil *W* to incandescence. This ignites the substance which gets burnt completely in the excess of oxygen provided inside the bomb. Since the oxygen is present under pressure, the combustion of the material is practically instantaneous.

The heat generated by the combustion raises the temperature of water contained in the calorimeter *P*. The water is very thoroughly stirred and the steady final temperature noted. Knowing the water-equivalent of the bomb, the heat of combustion is easily calculated.

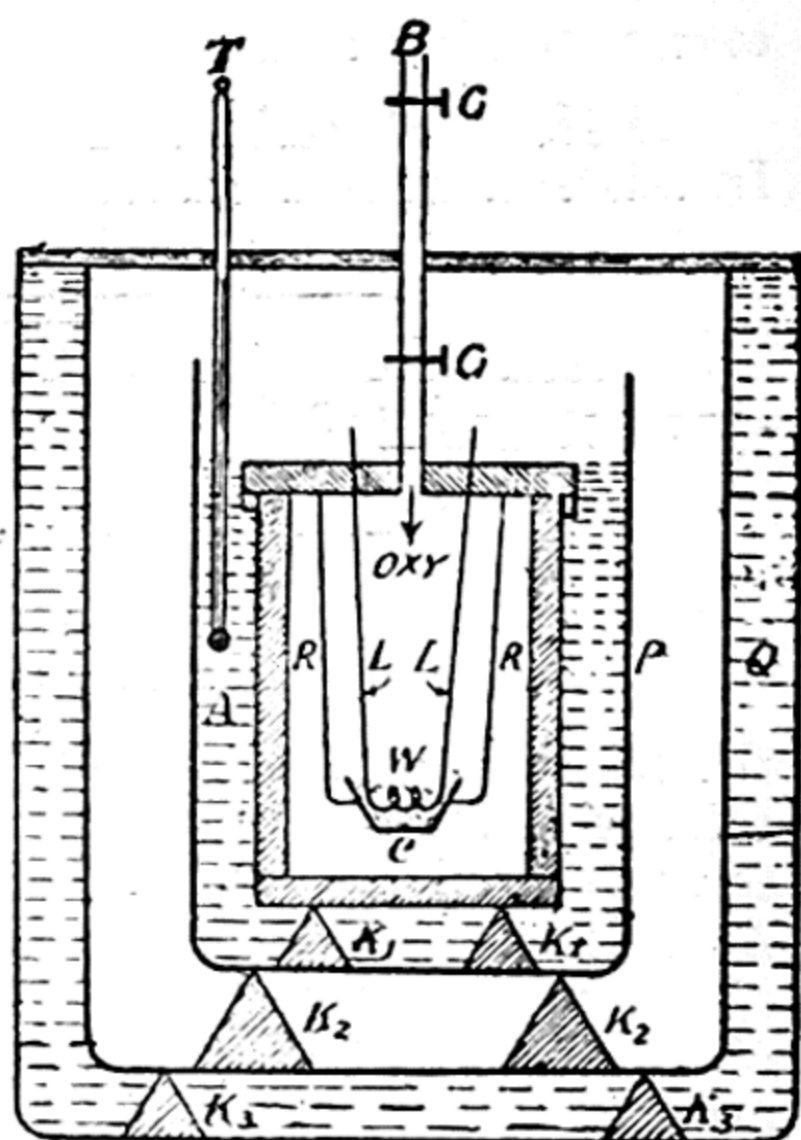


Fig. 3.12. Bomb Calorimeter.

To avoid losses of heat from the surface of the calorimeter P , it is surrounded by a constant-temperature water jacket Q , as shown.

If the substance under test happens to be a gas, a known weight of the gaseous fuel is mixed with an excess of oxygen and is then compressed into the bomb. When the wire W is heated, the mixture explodes. The crucible C is not needed in this case.

Calorific Value of some fuels :—

Fuel	Cal. per gm.
Anthracite coal	8,800
Gas coke	6,000
Petrol	11,400
Paraffin oil	16,200

3.17. Calorific value of food. The quantity of food needed by a man depends upon his occupation. A labourer needs much more food than a clerk. A man can put out only as much energy as he takes in. Food-energy is measured in major Calories. A major Calorie is the heat required to raise the temperature of 1 Kgm. of water through 1°C .

1 major Calorie = 1000 calories.

A pound of food is said to contain as much energy as it would yield when completely oxidized. A person who works hard physically needs 4000–5000 major calories of food-energy per day, a clerk about 3000 or less.

Table of food-values.

Food	Major Calories per lb.
Mutton	1,200
Fish	360
Egg	600
Milk	300
Butter	3,500
Cheese	1,900
Rice	1,600
Wheat flour	1,600
Cabbage	120
Onions	200
Potatoes	300
Tomatoes	100
Apples	200
Bananas	300
Almond	1,600
Chocolate	2,800
Cocoa	2,200
Sugar	1,800

Acc. 4698.

3.18. Negative Sp. Heat of Saturated Vapours. The specific heat of a saturated vapour is the amount of heat that must be

supplied to a unit mass of it to raise its temperature by 1°C , *keeping it just saturated throughout the process*.

When the temperature of a mass of saturated vapour is raised, the vapour must be compressed in order that it may remain saturated, otherwise it will tend more and more towards unsaturation. During this process of compression work must be done on the vapour, but compression itself will heat up the vapour and the heat thus produced may be sufficient, or more than sufficient, to produce the requisite rise of temperature. In the latter case, heat will be given out by the saturated vapour as its temperature is raised, and consequently its *sp. heat is said to be negative*. Thus, saturated steam possesses a negative sp. heat at ordinary temperatures and therefore when it is allowed to expand adiabatically a partial condensation occurs. On the other hand, if a mass of saturated steam be compressed adiabatically, it ceases to be saturated. Although its pressure is considerably increased during the compression, no water is formed because the temperature is raised so much by the act of compression that the pressure attained is below the saturation pressure corresponding to the new temperature. Hence to keep the steam saturated, heat must be withdrawn from it when its temperature and pressure are increased. This shows that the specific heat of saturated steam is negative.

3.19. Dulong and Petit's Law. It states that the product of atomic weight and specific heat at constant volume is the same for all elements in the solid state and equals 6 nearly. This product is called *Atomic Heat* of the element. It is the thermal capacity of a gram of the substance and is proportional to the thermal capacity per atom, because one gram-atom of all elements contains the same number of atoms.

Table of atomic heats at ordinary temperatures.

Element	Atomic weight	Sp. heat	Atomic heat
Aluminium	27.0	0.212	5.72
Arsenic	74.9	0.083	6.22
Boron	10.8	0.307	3.32
Cadmium	112.4	0.055	6.13
Carbon	12	0.160	1.92
Copper	63.6	0.091	5.79
Gold	197.2	0.031	6.11
Iron	55.8	0.110	6.12
Lead	207.2	0.300	6.21
Nickel	58.7	0.109	6.40
Silicon	28.1	0.182	5.11
Silver	107.9	0.056	6.04
Tin	118.7	0.054	6.31
Zinc	65.4	0.92	6.02

This result can be deduced from kinetic theory which gives a value 5.96 for the atomic heat—a result not very different from 6: Since atomic weight of a substance is a constant quantity, it follows

that the various elements will have the same specific heat at all temperatures. This is however, contradicted by experiment. In fact, experiment shows that *the sp. heat of all substances changes with variations in temperature*. It decreases with falling temperature and tends to a zero value as the absolute zero of temperature is approached. On the other hand, with a rise of temperature, sp. heat also increases. Thus Weber showed that the sp. heat of diamond increases three-fold when it is heated from 0°C to 200°C .

Carbon, Boron and Silicon whose atomic heats at ordinary temperatures are 1.92, 3.32 and 5.11 respectively show an increase in these values towards 6, as their temperature is raised. Thus Nernst and Lindemann obtained the following values for the atomic heat of diamond (carbon) at various temperatures,

Temperature (Degrees Absolute)	Atomic heat
30	0.00
88	0.03
205	0.62
262	1.14
358	2.12
413	2.66
1169	5.45

A somewhat satisfactory explanation of the variation of sp. heat of elements with temperature has been given by Einstein and by Debye in term of the **Quantum Theory** which states that *energy is not emitted or absorbed by matter continuously but in discrete amounts or quanta*. According to the Debye's theory of sp. heats.

(1) the atomic heat will increase with temperature and tend to the value 6.

(2) the atomic heat will decrease as the temperature falls and tend to zero at absolute zero.

Near about the absolute zero of temperature, the sp. heat of a substance is proportional to the cube of the temperature (in degrees Absolute). This relationship is known as Debye's T^3 law.

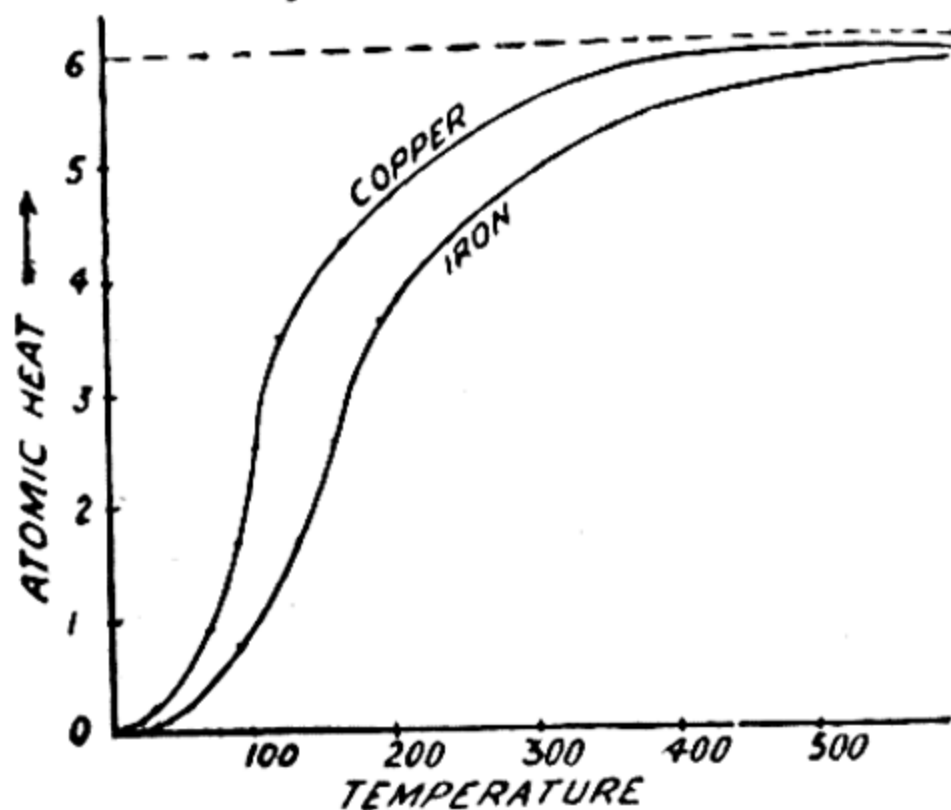


Fig. 3.13.
Variation of atomic heat with temperature ($^{\circ}\text{A}$)

(3) The general nature of the curve showing the variation of sp. heat with temperature is the same for all substances. Any two curves can be made to coincide with each other by suitably adjusting the scales of one of them.

3.20. Total Heat of Steam. Since the boiling point of a liquid depends upon pressure, Regnault produced steam at various temperatures by putting the boiler in communication with a pressure chamber and showed by actual measurements that latent heat of water diminishes with a rise in temperature.

The total heat of steam at $t^{\circ}\text{C}$ is the quantity of heat that must be supplied to one gram of water, initially at 0°C , in order to convert it into saturated vapour at $t^{\circ}\text{C}$. The total heat is the sum of the heat required to warm up one gram of the water to t° (*i.e.*, t cal), and the latent heat L_t .

or
$$Q = t + L_t \quad (1)$$

Regnault found as a result of his experiments that

$$Q = 606.5 + .305t$$

\therefore from (1)
$$L_t = 606.5 + .305t - t = 605.5 - .695t.$$

i.e., the latent heat of vaporization decreases with rise of temperature. Thus at 100°C

$$L_{100} = 606.5 - .695 \times 100 = 537 \text{ cal. per gm.}$$

and at a temperature t , equal to $\frac{606.5}{.695} = 872^{\circ}\text{C}$ the latent heat of vaporization of water would be zero.

3.21. Spheroidal State. When a little liquid is placed on a metallic surface heated to a sufficiently high temperature, it collects itself into a spheroidal drop which is separated from the metallic surface by a cushion of its own vapour. The size of the drop gradually diminishes due to evaporation from its surface as heat reaches the drop across the vapour by conduction. Lack of contact between the liquid and the plate can be shown by immersing in the liquid one terminal from an electric battery and joining the other terminal to the plate, when it will be observed that a galvanometer connected in the circuit registers no current. A beam of light can also be sent across the cushion of vapour, this also shows a lack of contact. When however the temperature of the plate is lowered, the liquid boils away violently.

3.22. Micro-calorimetry. In recent years a special branch of calorimetry, called **Micro-calorimetry** has been developed. It deals with very small thermal effects met with in Physics (*e.g.* heat developed in natural and artificial radio-activity), in Physical Chemistry (*e.g.* heat evolved by the adsorption of gases), in Metallurgy (*e.g.* heat evolved during slow crystallization of metal alloys), and in Biology (*e.g.* heat evolved by a growing plant, by bacteria and by germination of seeds) etc. Some of these thermal processes are of very short duration while others last for years.

Although Bunsen's Ice Calorimeter can be used to measure thermal phenomena of long duration, unfortunately 0°C of temperature is much too low a temperature for measuring the heat produced during numerous chemical reactions. Real progress in this direction

CALORIMETRY

was only made when Richards and others introduced the **Adiabatic Calorimeter**. It is so arranged that the temperature of the jacket surrounding the calorimeter is equal to the temperature of the calorimeter itself, throughout the duration of the experiment. Under these circumstances no exchange of heat can take place between the calorimeter and its surroundings and the error associated with radiation of heat between the calorimeter and jacket is eliminated or at least reduced considerably.

The whole apparatus is located in a constant-temperature room. It is usual to maintain the room 3° — 5°C above the temperature of the rest of the building, using a thermostat for the purpose and keeping the fluctuations of temperature within $\pm 0.001^{\circ}\text{C}$.

In most micro-calorimetric measurements, the temperature-increases are of the order 0.1° to 0.2°C per hour and are sometimes much lower. But it is not difficult to maintain a proper heating of the jacket. To measure such temperatures, special thermopiles having a large number of thermocouples are used.

QUESTIONS

1. Show that a gas possesses two specific heats. Give the Regnault's method for determining sp. heat at constant pressure.
2. Explain with a clear sketch Jolly's method for finding the sp. heat of a gas at constant volume. State the precautions and the corrections to be made.
3. Explain the continuous flow method of determining C_p . What are its chief merits?
4. Write short notes on (i) Negative sp. heat of saturated vapours (ii) Total heat of steam (iii) Dulong and Petit's Law (iv) Spheroidal State. (v) Bomb calorimeter (vi) Micro-calorimetry.
5. The temperature of a body falls from 40° to 20°C in five minutes. The air temperature is 13°C . Find the temperature of the body after a further 5 minutes. [15.88°C]
6. What do you mean by 15° calorie and mean calorie. Describe the Bunsen's Ice Calorimeter method for determining specific heats. What are the chief merits of this arrangement.
7. Describe the metal block calorimeter method for determining specific heats. Why is it preferred to the usual 'method of mixtures'?
8. Does the sp. heat of a substance depend upon its temperature? How will you determine the sp. heat of (i) a metal (ii) non-metal at the temperature of liquid-air.
9. Explain 'Law of Cooling'. How can it be used to determine specific heats of substances. Can the method be used for solids.
10. Write a careful note on Dulong and Petit's Law of Atomic Heats.

CHAPTER IV

VAPOUR AND VAPOUR PRESSURE

The ultimate aim of science is to discover as much as is discoverable about the reality behind the phenomena.

— *deSitter*.

4.1. Vapour. The term **vapour** is applied to the gaseous condition of these substances which, like water, alcohol, etc., are liquids at ordinary temperatures. There is, however, a fundamental difference between gases and vapours. A vapour can be liquefied by a suitable compression alone, but no increase of pressure, howsoever great, will succeed in liquefying a gas. If, however, the gas be cooled below its critical temperature¹ (which is different for different gases), it will liquefy just like a vapour. A gas is thus always *above* its critical temperature while a vapour is always below it.

A vapour exerts pressure. This can be shown by introducing a liquid, drop by drop, into a barometer tube with the help of a curved pipette. Successive drops of the liquid rise up the mercury column, disappear on reaching the top and at the same time depress the mercury column. A stage is ultimately reached when the last drop of liquid merely floats on the surface and no further lowering of the mercury column takes place. The space is now said to contain *saturated vapour*. It exerts the maximum pressure for that temperature. The density of such vapours is also a maximum; if a barometer tube holding a saturated vapour be depressed in a mercury trough, a partial condensation of the vapour will take place. A vapour in contact with its own liquid in a closed space is always saturated.

4.2. Laws of Vapour Pressure. The maximum vapour pressure exerted by a liquid

(1) depends upon temperature; the higher the temperature the greater the pressure.

(2) depends upon the nature of the liquid; the more volatile the liquid the larger is its pressure for a given temperature.

(3) is independent of the volume of the space available for evaporation; more liquid evaporates in a larger space and less in a smaller space but the maximum pressure exerted is the same in either case.

(4) is the same whether its vapour is present alone in a given space or some other vapour is already present there. In the latter case

1. It is that temperature above which a gas cannot be liquefied by any increase of pressure whatsoever.

evaporation will be slower but the final pressure reached will be the same as in the former case.

(5) The total pressure exerted by a number of vapours in a closed space is the sum of the partial pressures which each vapour would exert if it were alone present, provided

- (a) the number of vapours present is not large, and
- (b) they do not react chemically with one another.

4.3. Unsaturated Vapour. A space contains unsaturated vapour if more of the liquid can evaporate in it at constant temperature. The density and the pressure exerted by such vapours are less than those for a saturated vapour at the same temperature.

Unsaturated vapours obey Boyle's Law fairly well when they are far removed from their points of saturation. If an unsaturated vapour be gradually compressed at constant temperature, its volume will decrease nearly in accordance with Boyle's Law, till the vapour becomes saturated. At this stage it will begin to liquefy and if the pressure were maintained, the whole of it would turn into the liquid form. Increasing the pressure any further will have no effect on it, because liquids are practically incompressible.

4.4. Measurement of Vapour Pressure. (1) *At Ordinary Temperatures.* It is determined by a method due to Regnault. Two identical tubes *A* and *B* are set up side by side in a basin of mercury. Their upper portions project into a water bath with a glass front. The bath can be warmed up to any desired temperature with a burner placed below it. It can be stirred from above and its temperature recorded with a sensitive thermometer. The experimental liquid is introduced into *A*, drop by drop, till no more of it vaporizes. The difference between the levels of mercury in the two tubes is the required vapour pressure.

At higher temperatures, the mercury will be depressed considerably because of increase of pressure. A deeper water bath will be needed which can neither be heated nor stirred efficiently.

(2) *At Low Temperatures.* The vapour pressure at low temperatures can be determined by a method due to Gay-Lussac. The tube *A* in this case is bent round at the top and ends in a small round bulb *C* containing the experimental liquid which can be cooled down to any desired temperature by surrounding it with a freezing mixture. The pres-

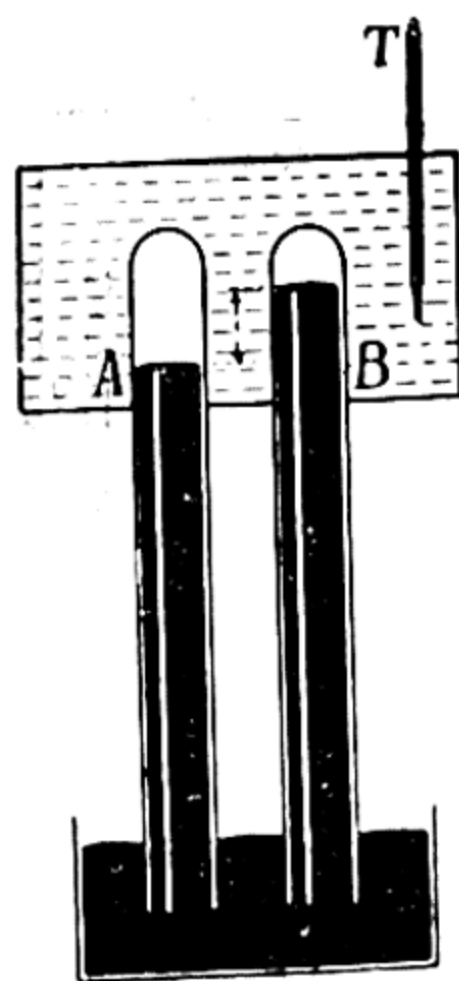


Fig. 4.1
Vapour pressure at ordinary temperature

sure of the vapour depresses the column in *A* and this lowering relative to *B* is the vapour pressure required.

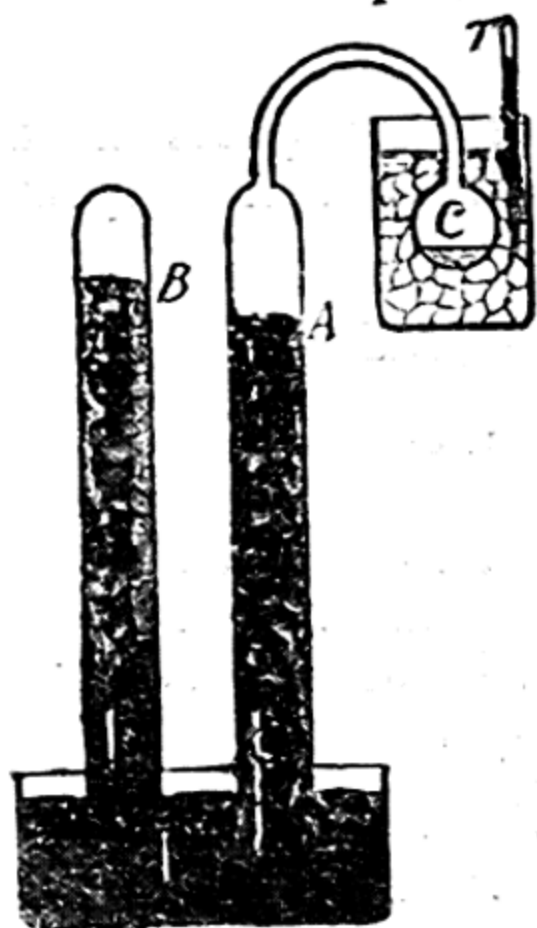


Fig. 4.2

Vapour pressure at low temperatures.

(3) *At High Temperatures.* This is determined by a method due to Regnault. Here the pressure on the liquid is changed by putting it in communication with a pressure chamber. The boiling point of the liquid can thus be changed. Instead of the temperature being the independent factor as in the former cases, it is here controlled by changes of pressure. Hence the method is sometimes called the *dynamical method*.

The experimental liquid is contained in a copper boiler *B*, whose temperature is recorded by mercury thermometers *TT* enclosed in steel tubes (not shown). The boiler is joined to a globe *G* placed in a constant-temperature water bath and filled with air. Any desired pressure can be produced in the apparatus by working the pump and the pressure thus produced can be measured with the manometer *M*. The vapours given off by the liquid are condensed by the water jacket *C* and returned to the boiler. This prevents any wastage of the liquid. By increasing the total volume of the apparatus, *G* absorbs the jerks that are produced

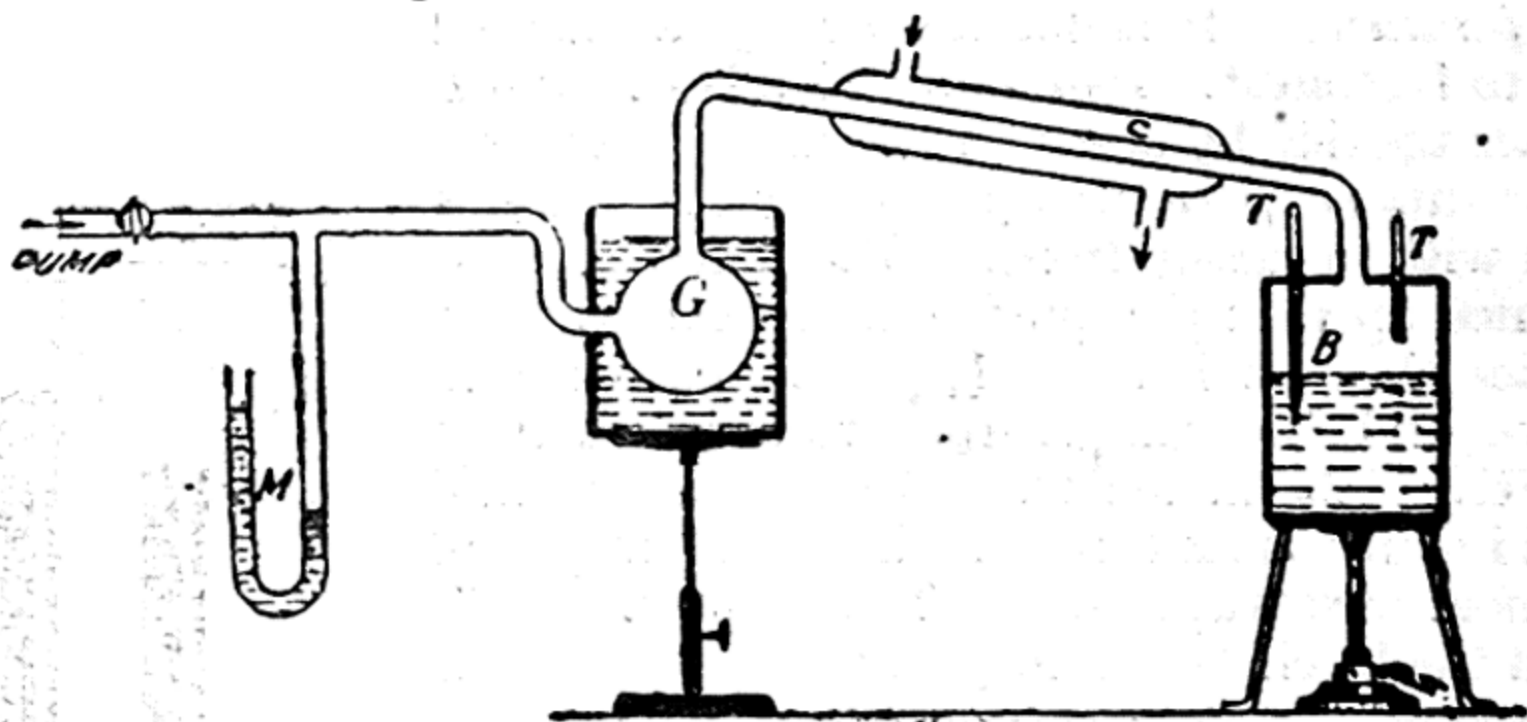


Fig. 4.3

Vapour pressure at high temperatures.

when the pump is worked. Moreover, it enables the pressure to be altered by small amounts. The pressure in *G* which is the same as in *B* is transmitted to the manometer which measures it.

4.5. Density of Saturated Vapours. The densities of vapours can be measured by the usual methods (Victor Meyer's or any other) given in junior chemistry books. The determination of the densities of saturated vapours, however, presents difficulties. The method selected should indicate the exact instant when the vapour is *just* saturated. If the temperature be slightly higher, the vapour will not be saturated and if it be lower, some liquid will be present along with the vapour.

The difficulty is overcome in a method due to Fairbairn and Tate. The apparatus consists of two glass globes provided at the ends of a tube bent twice at right angles, as shown. The bent tube is filled with mercury while the bulbs *A* and *B* contain different amounts of the experimental liquid and its vapours only, all air having been sucked out. *Since the pressure of a saturated vapour depends on temperature only, it will be the same in both the bulbs.* The level of mercury in *A* will be slightly lower than that in *B* on account of the difference in the weights of the liquid in the two bulbs.

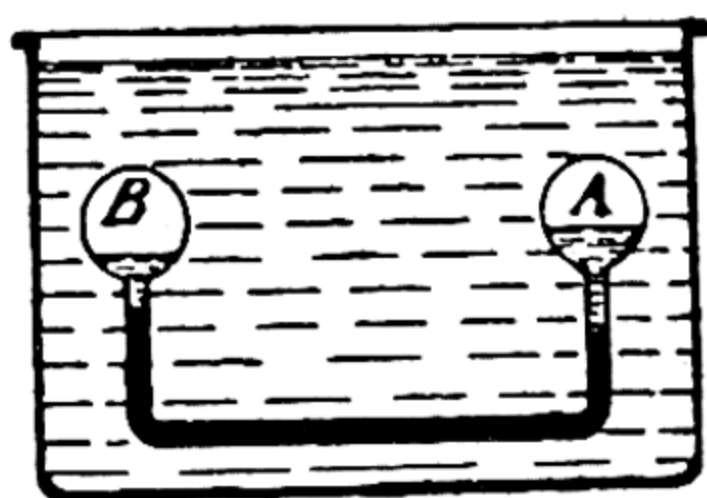


Fig. 4.4 Fairbairn and Tate's Apparatus

The whole apparatus is placed in a water bath and gradually heated. The liquid in both the bulbs gradually evaporates but the vapour pressure remains the same in both of them as long as any liquid remains in *B*. Just at the moment when all the liquid in *B* has vaporized, a slight increase of temperature will make the vapour in it unsaturated and since the pressure exerted by an unsaturated vapour is less than that exerted by the saturated vapour at the same temperature, a marked difference of levels is suddenly produced. If the mass of the liquid in *B* is known, density at the temperature is at once found out. By enclosing different amounts of the liquid in *B*, the density of the saturated vapour can be found at various temperatures.

It has been found that near the point of saturation vapours are much more compressible than is demanded by Boyle's Law. Fairbairn and Tate found that the density of saturated steam is greater than that given by Boyle's Law. Careful experiments by later workers have shown that the results obtained by Fairbairn and Tate are not quite satisfactory since condensation or absorption of vapours occurs on the walls of the bulbs. Thus Fairbairn and Tate determined that a gram of saturated steam at 100°C and 76 cm. pressure occupies 1641 c.c. while later workers have found it to be 1677 c.c.

4.6. Fusion. It is the passage of a solid into its liquid state. Fusion occurs when due to an increase in the molecular motion, the force binding the molecules together, is weakened. Since this cohesive force is different for different substances, the temperature at which this force gets sufficiently weakened to make the change of state possible will be different for different substances. In other words, each substance has its own definite melting point.

Pure crystalline solids have very sharp melting points. When such a solid is heated, a temperature is reached at which it changes *sharply* into liquid. This is the *melting point* of the substance and it has a definite value for each substance depending upon the external pressure. Conversely, if the liquid obtained be now cooled, solidification sets in at the same temperature, if external pressure remains the same. For pure crystalline substances, *Melting point and Freezing point are identical.* Impure substances, mixtures and amorphous substances do not have sharp melting points. *Fusion is always accompanied*

by a change of volume. Some substances, like wax, expand or increase in volume on melting (*i.e.*, the solid form is the denser of the two). In other cases like ice, the substance contracts on melting (*i.e.*, the liquid form is the denser of the two).

4.7. Effect of Pressure on melting point. The effect of a change of pressure on the melting point of a substance depends upon whether the substance expands or contracts in volume during melting. It is easy to see that for a substance like ice, which contracts on melting, increase of pressure will help the contraction to take place and therefore make it easier for the solid to melt *i.e.*, melting will occur at a lower temperature or *melting point will be lowered on an increase of pressure*. On the other hand, for a substance like wax, which expands on melting, increase of pressure will hinder this expansion from taking place, with the result that melting will take place with difficulty *i.e.*, *melting point will be raised on the application of pressure*. All this can be discussed very easily with the help of Clapeyron's equation (Article 12.9).

4.8. Boiling or Ebullition. Every liquid begins to boil when it is heated to a certain definite temperature (which is different for different substances) under a given external pressure. This temperature is as characteristic of a pure liquid as is the melting point for a pure solid. In fact, these temperatures are used to identify substances.

Every liquid exerts a vapour pressure which increases as the temperature rises. *At the boiling point of a liquid, its vapour pressure is equal to the atmospheric pressure*. Since the vapour of a liquid always occupies a much greater volume than the liquid, the effect of an increase of pressure is to hinder this expansion from taking place or in other words, *increase of pressure always raises the boiling point*. (Article 12.9).

4.9. Elevation of boiling point. A solution is a homogeneous mixture of two or more components. The component which is present in larger amount is called the *solvent* while the dissolved substance is called the *solute*.

When a non-volatile solute is dissolved in a solvent the vapour pressure of the latter is lowered. Van Babo found that for any given solution, the decrease of vapour pressure from that of the pure solvent is a constant fraction of the vapour pressure of the solvent, for all temperatures. Thus if p be the vapour pressure of the pure solvent and p' , that of solution, $(p-p')/p$ is a constant for any given solution for all temperatures. Later Wullner found that the lowering of the vapour pressure was proportional to the concentration of the solution and Raoult showed that

$$\frac{p-p'}{p} = \frac{n_2}{n_1+n_2}$$

where n_1 are the number of mols. of solvent and n_2 , those of the solute.

Since the vapour pressure of a solution is less than that of the pure solvent, the vapour pressure of the solution will equal the

atmospheric pressure at a higher temperature. In other words, the solution will boil at a temperature higher than that of the pure solvent. The determination of the elevation of the boiling point enables us to determine the molecular weight of the dissolved substance.

4.10. Depression of the Freezing Point. When a non-volatile solute is dissolved in a solvent, the freezing point of the solution is lower than the freezing point of the pure solvent. Blagden has shown that the lowering of the freezing point of a solution is proportional to the concentration of the solution. The comprehensive work of Raoult has shown that equimolecular solutions of different substances of similar type lower the freezing point of a given solvent to the same extent. The freezing point of the pure solvent is that temperature at which the solvent is in equilibrium with its solid form, while the freezing point of a solution is the temperature at which it is in equilibrium with the pure solid solvent. The former temperature is higher than the latter and the difference between the two gives the depression of the freezing point. This depression also enables us to determine the molecular weight of the dissolved substance.

4.11. Triple Point. (1) The boiling point of water depends upon pressure; it is raised when the pressure is increased and *vice versa*. The relation between temperature and pressure can be represented by the curve AB which is called the *Steam-line*. The liquid and vapour are in equilibrium only along the line AB ; thus if the pressure be increased at the point P (keeping temperature constant) all vapour will condense and only liquid will remain and if the pressure be decreased all the liquid will vaporize. Therefore, only the liquid is present at all points above AB and only the vapour below it.

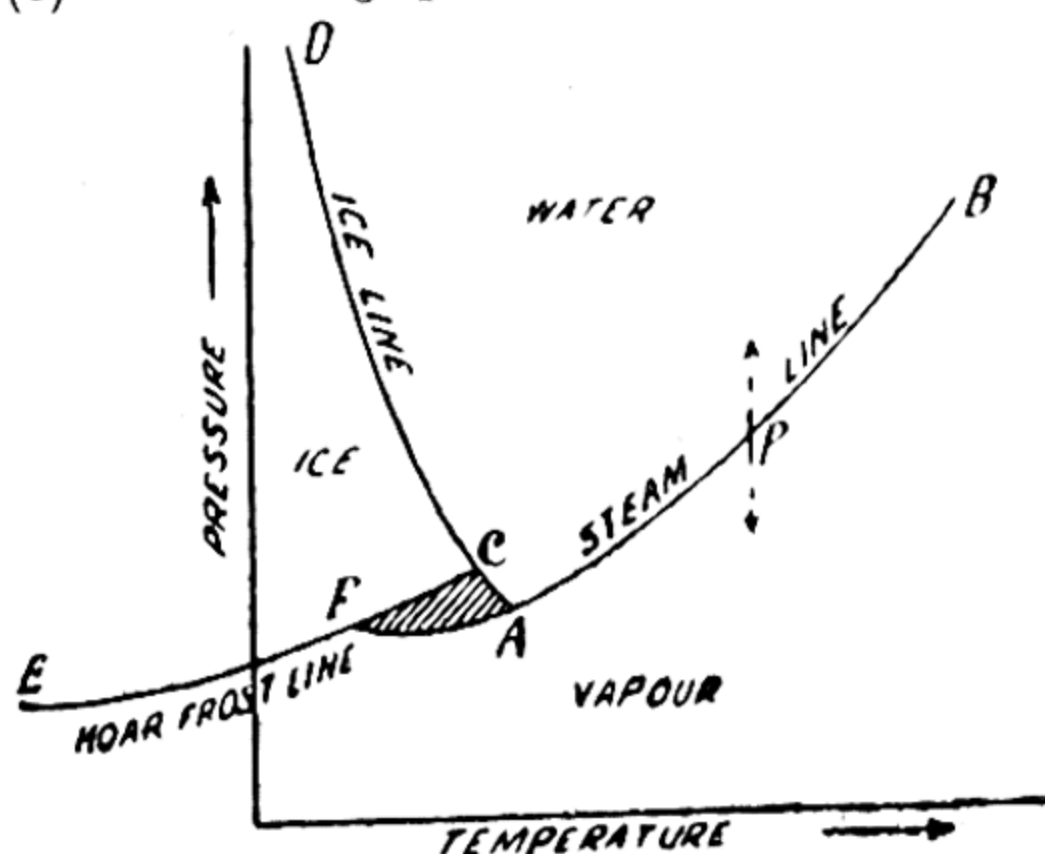


Fig. 4.5
Triple point (1)

(2) Again, the melting point of ice is lowered on increase of pressure, *i.e.*, ice melts below 0°C when subjected to a pressure greater than the atmospheric, but the melting point is raised when the pressure is decreased. The relationship between pressure and temperature for ice can be represented by the line CD called the *Ice-line*. It is all water to the right of it and all ice to its left.

(3) Evaporation goes on all temperatures. It is helped by a decrease of pressure and *vice versa* *i.e.* when the pressure on ice is increased evaporation from its surface slows down. The equilibrium

between ice and vapour can be represented by the line EF called the *Hoar-frost line*. It is all ice above EF and all vapour below it.

Thomson put forth the view that the three curves—the steam line, the ice-line and the hoar-frost line meet at one point called the **Triple point**. *At the triple point, the solid, liquid and gaseous states, all exist simultaneously in perfect equilibrium.* The triple points of most substances lie at pressures which are low compared with the normal atmospheric pressure.

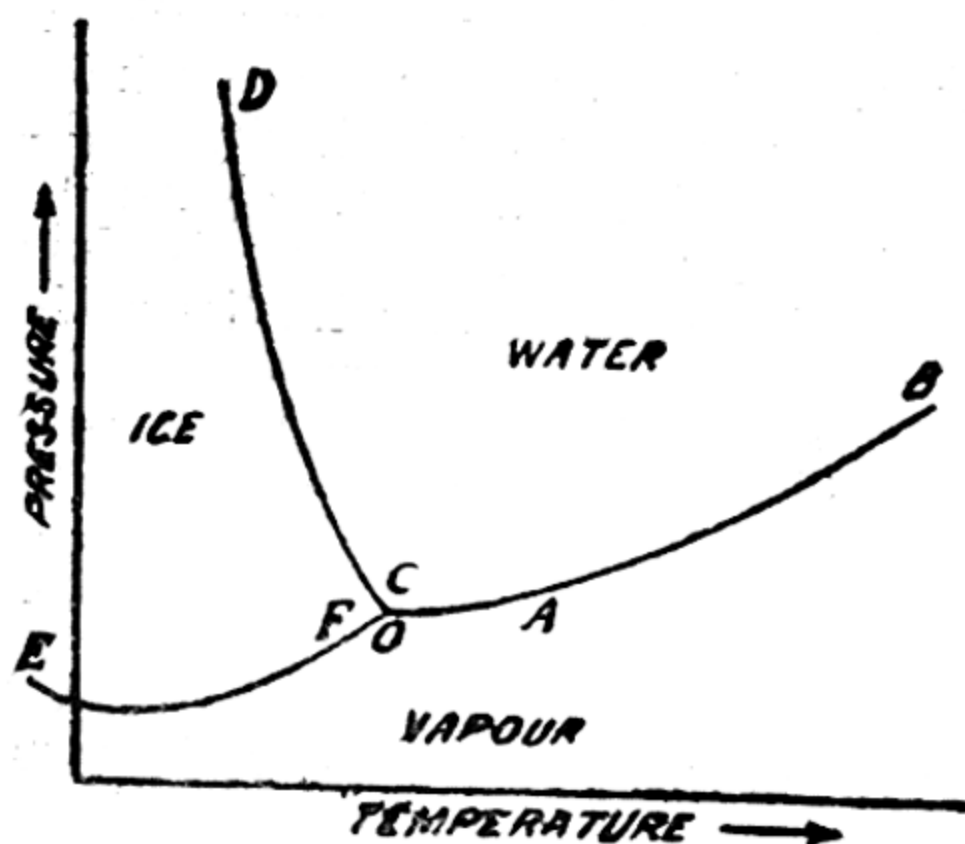


Fig. 4.6
Triple Point (2)

It is easy to show that the three curves must meet in a point; if they intersected as shown in the diagram (1) then the shaded portion must represent only the liquid state since it is above AB , only the solid state since it is below CD and only the vapour state since it is below EF . These conclusions contradict one another, hence the three curves must meet in a single point O . The pressure corresponding to the triple point is 4.6 mm. of mercury while the corresponding

temperature is about $+0.00716^{\circ}\text{C}$. Since there are various allotropic modifications of ice, this triple point is by no means the only one for water.

It is clear from fig. 4.6 that if a vapour has a pressure below its triple point value and its temperature be sufficiently reduced it will pass from the region A to F , i.e. the vapour will condense directly to solid. Conversely, a solid will be converted directly into its vapour (i.e. sublime) when its temperature is raised, provided its vapour pressure remains below that corresponding to its triple point. Thus iodine (Triple point temperature 114°C and vapour pressure 90 mm.) shows the above effects.

4.12. Gibb's Phase Rule. Consider water at the Triple point O (Fig. 4.6). Here ice, water and vapour of water exist in equilibrium i.e. they cannot alter with time without gain or loss of energy. Considered separately, each part—ice, water, or vapour is homogeneous in itself and is called a **Phase**¹. The *phases of a system* refer to its homogeneous parts separated from one another by definite physical boundaries. Thus ice, water and vapour are the three phases in the water system.

Now consider the space DCB . If we limit our discussion to this space and do not over-step its boundaries, we can change the pressure and temperature independently to any values we like and water will remain a liquid. We express it by saying, that in the space DCB ,

1. Phase literally means 'form or appearance'.

the system (water) possesses two **Degrees of freedom** (pressure and temperature). Similarly ice in the space *EDC* and vapour in the space below *ECB* possess two degrees of freedom each.

Now consider the line *CAB*. Along this line vapour is in equilibrium with water. If we change the temperature to a new value, pressure will automatically adjust itself to this new temperature (\therefore vapour pressure depends upon temperature), or in the alternative, if we adjust the pressure, temperature automatically adjusts itself. Both pressure and temperature cannot be adjusted independently of each other. In other words, the system, liquid-vapour, possesses only one degree of freedom.

At the triple-point *O*, the system, solid-liquid-vapour, possesses zero degrees of freedom. If we change either pressure or temperature one of the phases will disappear.

By **Degrees of Freedom**² of a system we mean "the number of variable factors, *e.g.*, temperature, pressure etc., which can be altered without destroying the nature or equilibrium of the system".

By **components** of a system we mean the number of distinct chemical species involved. Thus in our illustration there is only one component *i.e.*, water, because both ice and vapour are not chemically different from it.

Gibb's Phase Rule states that the sum of the number of phase (*P*) and the number of degrees of freedom (*F*) is always equal to the number of components (*C*) involved, plus two. Or

- (i) for the system, liquid,
- (ii) for the system liquid-vapour
- (iii) for the system solid-liq-vap.

$$\begin{aligned}
 P + F &= C + 2 \\
 1 + 2 &= 1 + 2 \\
 2 + 1 &= 1 + 2 \\
 3 + 0 &= 1 + 2
 \end{aligned}$$

The phase rule asserts that the number of phases may at most be greater by two than the number of components. A system consisting of a single substance, *e.g.* water, can at the most have three phases.

4.13. Cooling curves provide an important method for studying phase changes in metals and alloys. Any change in state or constitution is accompanied by an energy-change which is shown by an evolution of heat during cooling or by an absorption of heat during a temperature rise. When a body cools without such a change, the cooling curve has the form I.

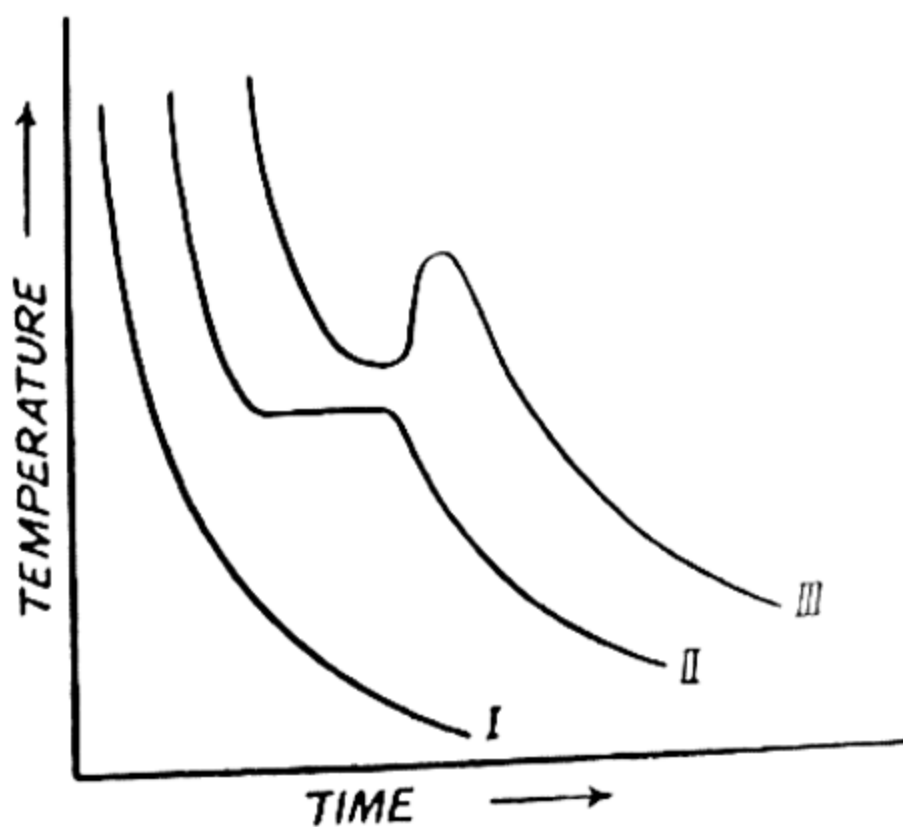


Fig. 4.7
Cooling Curves

If the substance is a molten metal,

2. The meaning of the term 'degree of freedom' is different in the kinetic theory of matter.

regular cooling is arrested by the heat evolved, while the metal solidifies and cooling curve has the form II *provided no super-cooling has taken place*. However, actually the beginning of solidification is always accompanied by a super-cooling. Nuclei do not become sufficiently stable to serve as starting points for crystallization until the melt has cooled to a temperature lower than the highest temperature at which solidification can occur. Hence *actual* cooling curves for pure metals have the form III.

QUESTIONS

1. Distinguish between saturated and unsaturated vapours. How does a vapour differ from a gas?

2. State and explain the laws of maximum vapour pressure.

3. How has the vapour pressure of liquids been determined at various temperatures. What is the objection in using the same method for all temperatures? Explain in detail.

4. What difficulties are experienced in determining the density of saturated vapours. How have they been overcome by Fairbairn and Tate? Are their results quite satisfactory? If not, what is the objection?

5. Write a brief note on Phase Rule. Explain clearly the meaning of phase, component and degree of freedom.

What information is supplied by cooling curves in studying phase changes in metals and alloys.

6. Write a short note on the Triple point of water.

CHAPTER V

HYGROMETRY AND AIR-CONDITIONING

Immerse yourself in the facts, especially the baffling facts, in the hope that illumination would come.—*Charcot*.

Physics takes its start from every-day experience which it continues by more subtle means.—*Schrodinger*.

5.1. Relative Humidity. Evaporation goes on all the time from water surfaces, but the amount of water vapour present in the air is very variable—a high temperature and good air-circulation promoting more rapid evaporation. Since the moisture-lifting capacity of air depends upon its temperature, it is possible that a sample of warm air may be holding considerable moisture and may yet be far removed from the saturation value, while, on the other hand, a sample of cold air may be holding much lesser moisture and yet may be practically saturated. Thus if an air-sample can hold a maximum of 10 gms. of water-vapour at say 30°C but is actually holding 4 gms. it is clearly far removed from saturation and is *dry*. On the other hand, if the sample can hold at 10°C a maximum of 5 gm. of water-vapour, but is actually holding 3.5 gms. it is very nearly saturated and is *damp*. Hence merely a knowledge of the actual amount of water-vapour held by a sample of air, is not by itself sufficient to enable us to classify the sample as damp or dry. In fact, it is clear from the above illustration, that a sample holding 4 gms. of moisture is dry while another, holding only 3.5 gm. is damp.

To get a correct estimate of the hygrometric state of the air, we must know.

(1) The amount of moisture, m , actually present in a given volume of air.

(2) The maximum amount of moisture, M , which the same volume of air can hold at the same temperature.

The ratio m/M is called **Relative humidity**. It is usually expressed as a percentage.

$$\text{Relative humidity, } h = \frac{m}{M} \times 100. \quad \dots(i)$$

Air is said to be damp if h is 50 or more, otherwise it is dry.

5.2. Hygrometers. Instruments used for measuring Relative humidity are called *hygrometers*. In the chemical hygrometer m is determined by passing a measured volume of atmospheric air through a U-tube holding calcium chloride and determining the increase in the weight of the tube. Next, an *equal* volume of air is bubbled through

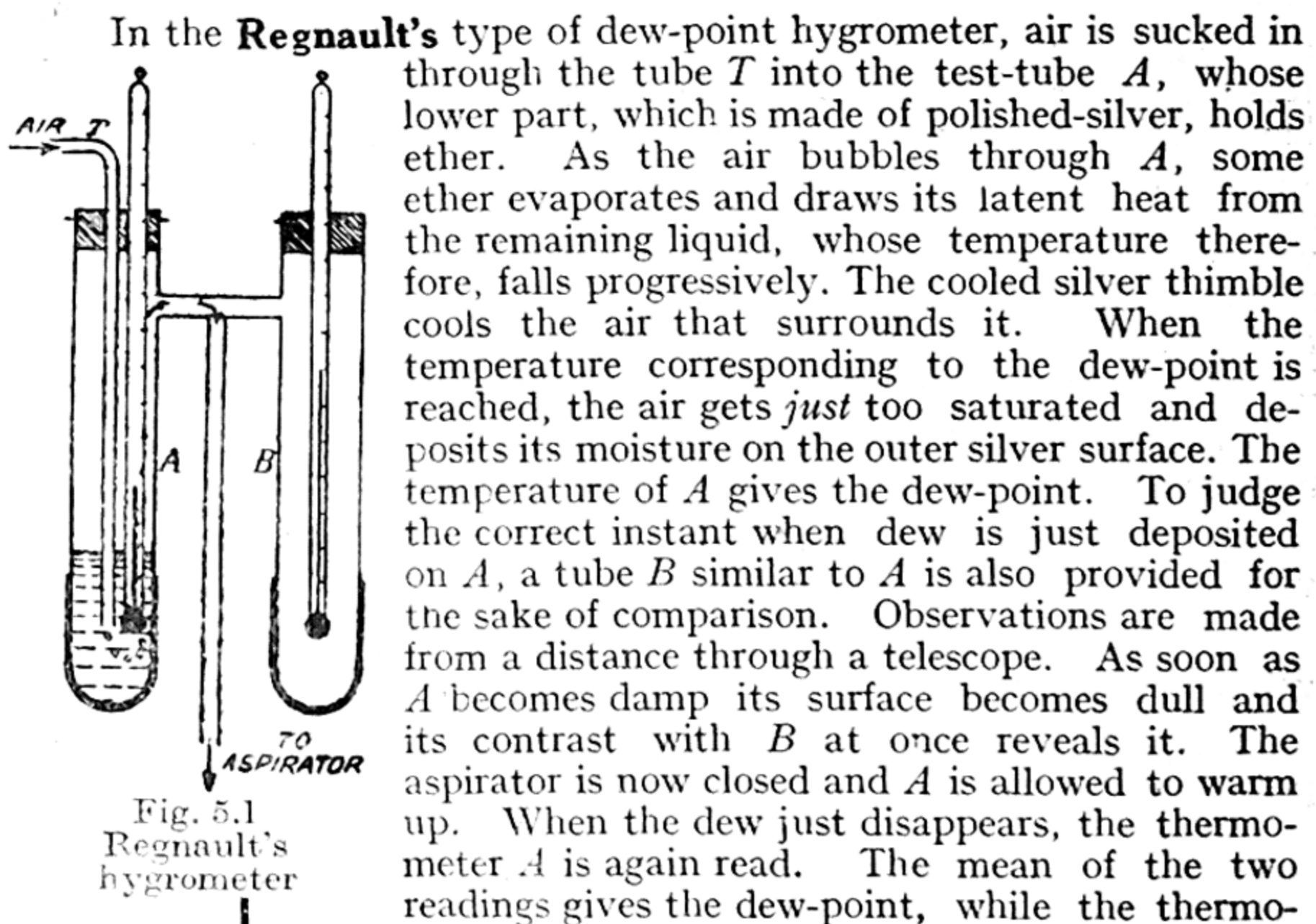
water at the *room temperature* and then sucked through the calcium chloride tube. The increase in the weight of the later gives M . ' h ' is determined using relation (i). This is a very accurate method of determining relative humidity, but as weighings are difficult to make and take much time, dew-point hygrometers are preferred.

In the **Dew-point hygrometers**, a small portion of the air, whose relative humidity is to be determined, is progressively cooled till at a certain lower temperature (called Dew-point) the amount of water-vapour actually present in it, is *just* sufficient to saturate it. The maximum vapour pressure at the dew-point is equal to the actual vapour pressure at room temperature. As the pressure exerted by a vapour is proportional to the mass of vapour present,

$$\frac{m}{M} = \frac{p}{P}$$

where p is the actual and P , the maximum vapour-pressure at the room temperature. Hence

$$\text{Relative humidity, } h = \frac{p}{P} \times 100 \quad \dots(ii)$$



When the temperature corresponding to the dew-point is reached, the air gets *just* too saturated and deposits its moisture on the outer silver surface. The temperature of A gives the dew-point. To judge the correct instant when dew is just deposited on A , a tube B similar to A is also provided for the sake of comparison. Observations are made from a distance through a telescope. As soon as A becomes damp its surface becomes dull and its contrast with B at once reveals it. The aspirator is now closed and A is allowed to warm up. When the dew just disappears, the thermometer A is again read. The mean of the two readings gives the dew-point, while the thermometer B indicates the room temperature. Humidity is calculated with the help of Tables that give maximum vapour pressures at various temperatures.

This arrangement fails if air be windy for, in that case unless the temperature is much lower than the dew-point, no moisture will get deposited on A .

5.3. Wet and Dry Bulb Thermometer. It consists of two mercury thermometers mounted side by side on a wooden or metal

plate. The bulb of one of the thermometers is covered with a pad of cotton gauze which can be wetted with water. Evaporation occurring at the wet surface lowers the temperature of the bulb. The drier the air, the greater is the cooling. The temperature of the dry bulb and that of the wet when its reading has become steady, are noted and relative humidity calculated with the help of Tables.

The reading of the wet bulb depends on the velocity with which air moves past it. It has been shown experimentally that if the air-velocity exceeds 3 meters per second the reading of the wet bulb is independent of wind velocity. Hence to get reliable results a ventilated type of wet and dry bulb thermometer is used. Air is driven past the thermometers by means of a fan driven by clock-work. Fig. 5.2 depicts an instrument called Assmann psychrometer.

5.4. Regulation of body temperature. To supply the energy needed for physical activity, the food we consume is burnt, the oxygen for the purpose being supplied by the air we inhale. To enable the body to maintain its normal temperature of about 98.4°F , the body must be able to lose the heat thus generated. Now, the amount of heat generated in a body and therefore the amount of heat to be lost by it, will depend upon the kind of activity a man is engaged in at the time. Thus a man lying comfortably in an easy chair loses about 80 major calories per hour, a man walking leisurely about 150 major calories per hour, a sedentary office-clerk about 100 per hour, while a man sawing wood loses about 300 major calories per hour. Such wide variations in the amount of heat lost are understandable when we consider that an active physical worker consumes a good deal of food. (1 major calorie = 1000 calories).

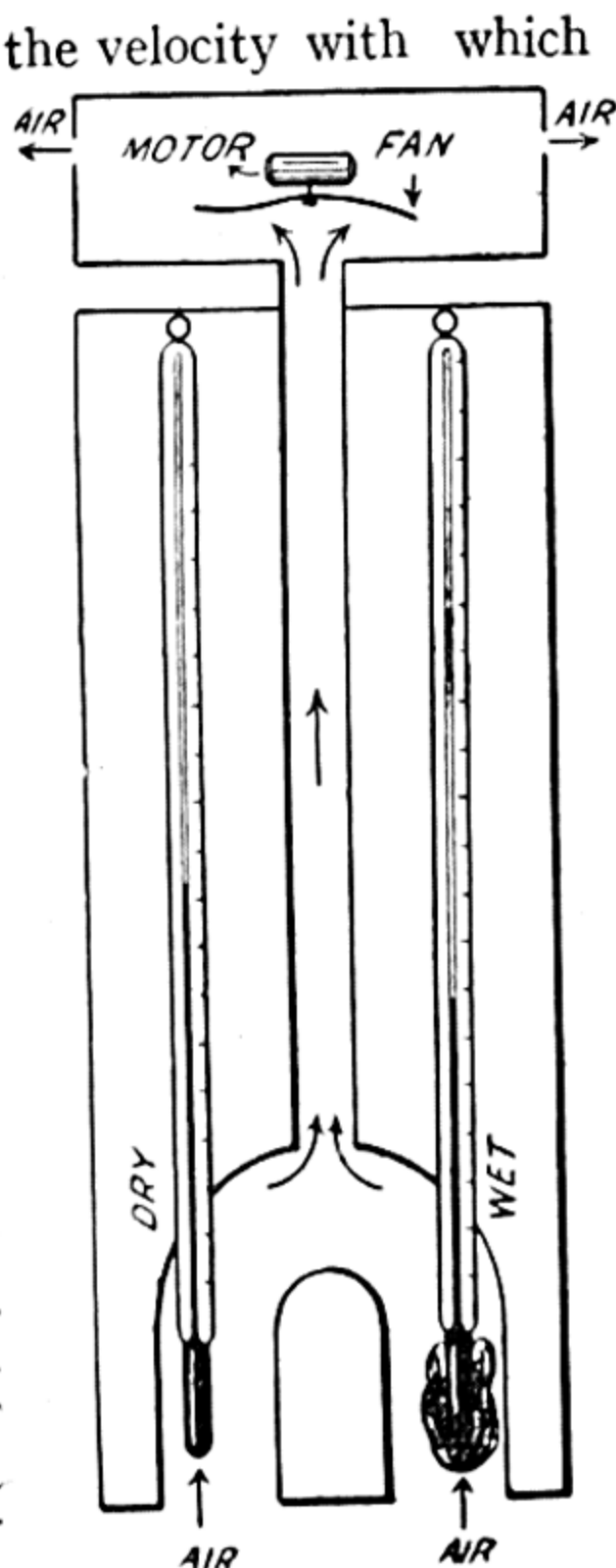


Fig. 5.2
Aspiration psychrometer.

But how does the body lose its heat? Heat is lost (i) by radiation from the skin, (ii) by convection currents in the air surrounding the body and (iii) by the evaporation of perspiration. The relative importance of the three factors is governed by the room-temperature and by the humidity. If humidity is high, evaporation will be slow. In this case the blood-capillaries near the skin get dilated, the skin temperature rises and heat is lost mostly by radiation and convection. If the room-temperature be higher than the body-temperature (98.4°F), the body will not be able to lose its heat by convection and radiation, but will lose all the heat by evaporation by increasing the activity of the sweat-glands, which will

make the perspiration flow towards the skin rapidly and its rapid evaporation at the skin will leave the later cool. If the humidity is high along with a high external temperature, the perspiration will not dry. Conditions very detrimental to health, now prevail and if they persist for any length of time, sickness may result.

5.5. Air-conditioning. We do not feel a sense of comfort and our efficiency is impaired if

- (i) air is too dry or too damp
- (ii) air is too hot or too cold
- (iii) air is stagnant or is in violent movement
- (iv) if dust and smoke particles or foul odours are present in the air.

If air is too dry it makes the skin crack. Dryness makes the mucous membranes of the lungs, nose and throat more susceptible to cold germs. Under proper hygrometric conditions people are less prone to catch cold. Proper ventilation makes the air we breath, fresh and invigorating. It is, therefore necessary, for good health and efficiency that the air of our dwelling-houses and places of work be 'conditioned'. In winter, the air must be warmed up and its moisture-content increased. In summer, the air must be cooled down and its moisture-content decreased. Again, in all seasons of the year, the air must be filtered to remove all its suspended impurities and should be properly circulated through the rooms. To add freshness some out-door air must always be mixed with the conditioned air. There must be 10 cubic feet of out-door air and 20 cubic feet of conditioned air circulated per minute per person.

In winter, humidity should range from 30 to 70% and the temperature from 63° to 71°F. In summer the humidity should range from 40 to 55% depending upon the out-door temperature and should be lower if the outdoor temperature is higher. The indoor *dew-point temperature* should be maintained constant at about 57°F whatever the outside temperature and the indoor temperature should range from 66°—75°F.

5.6. How Buildings are Air-conditioned. (1) *In Winter.* Air is drawn in by a blower through a duct covered by a fine gauze-filter, over heated furnace-surfaces and circulation is caused by the warmed-up air rising from the furnace to the room and cooler and heavier room air falling back to the furnace. By means of water-sprays air is humidified in the ducts. Arrangements are also made in the duct for drawing in quantities of fresh outside air.

(2) *In Summer.* Air is drawn in as usual through a gauze-covered duct but it is cooled by placing coils in the main duct and connecting them to a refrigerating machine. The air is de-humidified, by reducing the temperature of air to below the dew-point temperature, when it unloads its moisture. This is the best method of de-humidification. Two other methods are (i) by using a suitable drying agent say ammonia or sulphuric acid which absorbs moisture, (ii) by adsorbing the moisture. The moisture clings to the surface

of the substance used, say, silica gel. Another portion of the air is bubbled through water so that it gets fully saturated with water-vapour. By mixing it with the de-humidified air in suitable proportions any desired humidity can be obtained. This air is now circulated in the room by means of a blower.

5.7. Self-contained Air-conditioner. It is completely enclosed in its own cabinet. It is usually equipped with a heating coil which may be connected to a hot water or to a steam-heating or an electric-heating device. The cooling coil is connected to a refrigeration machine also housed within the container. If the refrigeration machine is air-cooled it must be placed in a window or in front of it, so that outdoor air may be used for carrying away the heat from the room. If it is water-cooled, it must be connected to a water-supply and a drain-pipe. It also contains a humidifier which must be connected to a water-supply line and a drain.

A fan draws the air into the self-contained air-conditioner through filters which remove dust and smoke etc. The air is then passed through heating and humidifying or cooling and dehumidifying apparatus. The conditioned air is discharged into the room at a high velocity so that it may be well-diffused to all parts of the room. A fresh-air connection is usually provided so that fresh outside air may be drawn into the air conditioner. This air is also filtered and conditioned before it is circulated.

5.8. Ammonia Ice Plant. It consists of a steel cylinder S containing ammonia gas in which a piston moves in and out. Two sets of coils—the compression coils C and the expansion coils E are connected to S through V_1, V_2 . A heat engine, called compressor, rotates the crank wheel A , the piston S is drawn out, the pressure of ammonia gas in the cylinder diminishes, the valve V_1 opens and ammonia from the expansion coils EE is sucked into the cylinder. When the piston moves inwards, ammonia gas gets compressed. This closes the valve V_1 but opens out V_2 and the compressed and heated ammonia moves into the compression coils C where it is cooled in a tank through which cold water circulates. This liquefies the ammonia which flows down under gravity and collects to the right of the regulating valve R . This valve has a fine hole in it through which a fine spray of liquid ammonia issues out to the left. As the gas pressure in EE is extremely low (practically all ammonia having been sucked out), the liquid ammonia at once evaporates drawing the latent heat from the brine tank B whose temperature therefore falls. As the machine works, the temperature of B goes on falling. It may fall to below -10°C . Tin-containers WW holding fresh water are placed in the tank B when the water in them gets frozen to ice.

The same plant may be used as a refrigerating machine for air-conditioning. The tank B is dispensed with and the coil E circulates round the duct which is drawing air into the room. In the alternative, the coil EE may be spread in the room along the walls etc. to cool the air. Ammonia-ice-machines are used for cold storage also *i.e.* for preserving perishable articles.

Although ammonia is the refrigerant usually employed, other refrigerants *e.g.*, carbon-dioxide and sulphur-dioxide are also used.

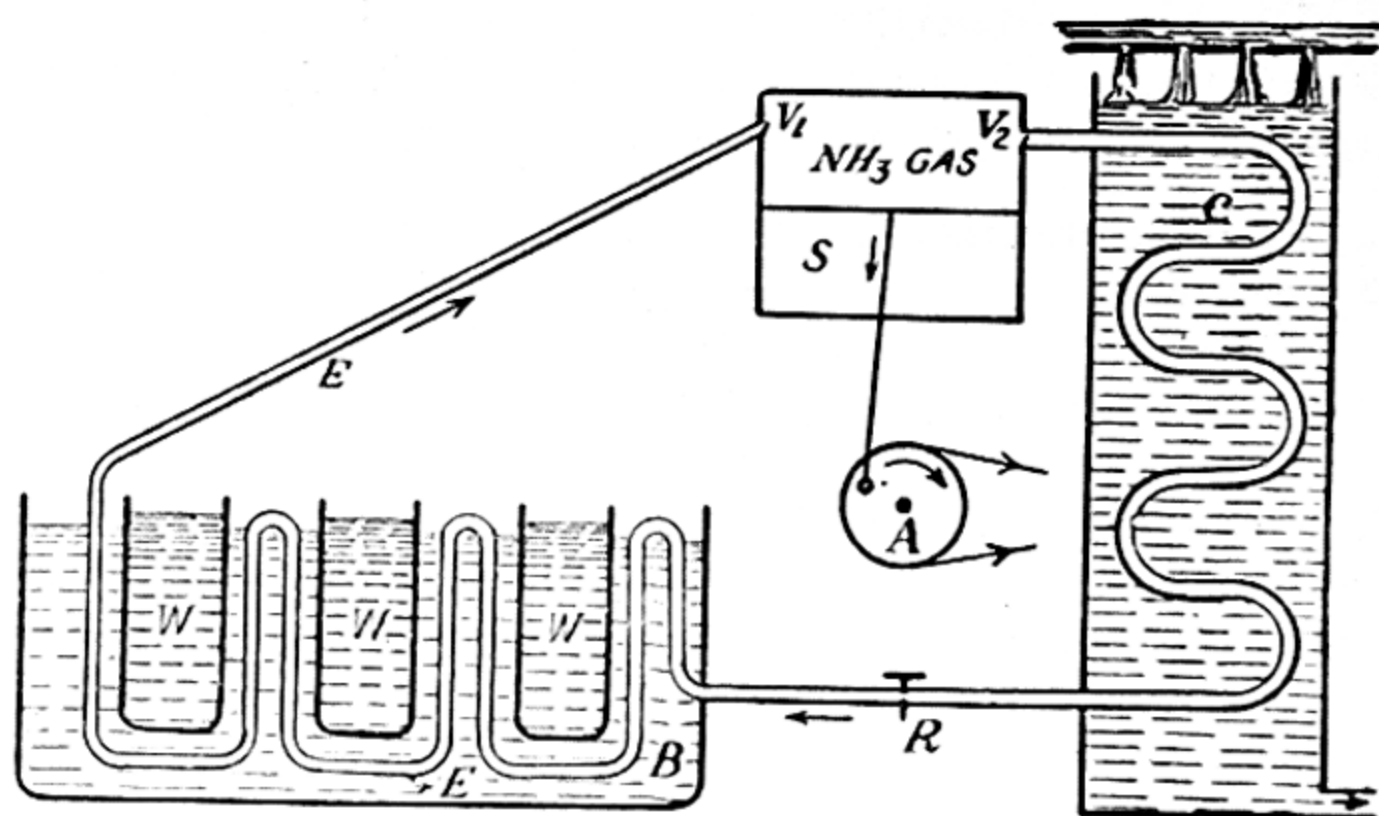


Fig. 5.3
Ammonia-Ice-Machine

The substance chosen in a particular arrangement depends upon the use to which the refrigerator is to be put. Carbon-dioxide requires a very high pressure, but the size of the plant is small, hence it is used on board ships. Nowadays Freon (CCl_2F_2) is also being used, especially for small refrigerators. In the small refrigerators the compressed gas is cooled by means of a fan provided for the purpose.

5.9. Electrolux Refrigerator. In the ammonia-ice machine, the liquid ammonia is evaporated by mechanical means (the outward movement of the piston creates a low pressure in the expansion coils, and this promotes evaporation). In the Electrolux, on the other hand, hydrogen gas is mixed with the ammonia, which reduces the partial pressure of ammonia below its saturation value and a rapid evaporation of ammonia liquid is thus favoured. The steel cylinder *D* containing a strong solution of ammonia is heated centrally either with an electrical heater *C* or with gas or oil. The dissolved ammonia is liberated in very large quantities, developing a high pressure, and rises up in *A*. It is cooled by the radiator fins and any water-vapour carried along by it is condensed and returned to *D*. At *E* the compressed ammonia is liquefied by the condenser and the liquid ammonia

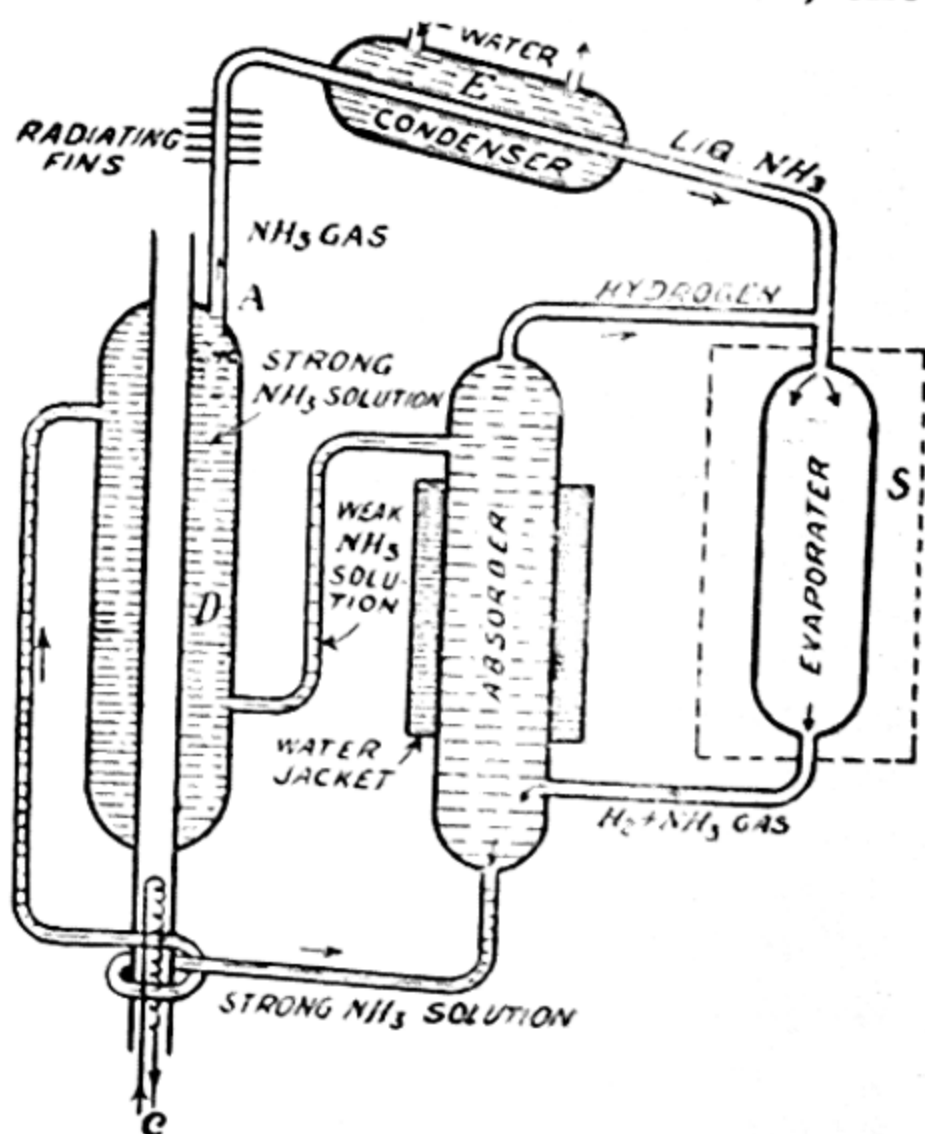


Fig. 5.4
Electrolux Refrigerator

flows towards the evaporator, in which hydrogen gas has a partial vapour-pressure of nine atmospheres. The apparatus is strong enough to withstand a total pressure of twelve atmospheres. *Since the partial pressure of ammonia in the evaporator is small*, the liquid ammonia at once evaporates, abstracting its latent heat from the space *S* which it is desired to cool. The temperature in *S* falls. The mixture of hydrogen and ammonia being heavier than hydrogen, sinks and reaches the absorber which is full of a weak ammonia solution. The ammonia dissolves while the hydrogen rises up and returns via *B* to the evaporator. To secure a better absorption of ammonia the absorber is water-cooled. The strong ammonia solution being heavier sinks and moves to *D*, where heating relieves it of most of the dissolved ammonia and the weak solution is returned to the absorber. No compressor is required in this case and the circulation of the liquid and gas is automatic. The apparatus is therefore very silent in working.

QUESTIONS

1. What factors determine the hygrometric state of air. Describe one method of determining relative humidity.
2. What is air-conditioning? Why is it resorted to? Explain in a general way, how a building may be air-conditioned (i) in winter (ii) in summer.
3. (a) Describe, giving a sketch, the working of the ammonia ice machine. For what other purposes may the machine be used?
(b) What properties should a refrigerating liquid possess?
[(i) It should have a large latent heat of evaporation.
(ii) The volume of its vapour should be small.
(iii) It should have a sufficient vapour pressure at the required temperature.]
4. Explain, giving a sketch, the working of an Electrolux refrigerator.
5. How is the human body able to regulate its temperature.

CHAPTER VI

MECHANICAL EQUIVALENT OF HEAT

The purpose of any physical theory is to explain as wide a range of phenomena as possible.—*Einstein*.

The pathway of science is littered with discarded ideas—ideas, which had to be worked out and tested, before the true could be known from the false.—*Cowling*.

6.1. Conservation of Energy. It is a well-known fact that heat can be produced by the expenditure of work. A gas can be warmed up by a sudden compression, a liquid can be heated by churning it or by forcing it through capillary tubes, a solid can be heated by hammering it or by rubbing one solid with another. The last method was, in fact, adopted by the primitive man to obtain fire. The reverse process is equally common. The sun's heat produces winds in the atmosphere which can be made to do mechanical work. The combustion of fuel in a heat-engine produces mechanical work. Even the early experiments of Hero had shown that motion may result from a heat transfer. It was the *quantitative* form given to these *qualitative* observations that led to the formulation of the Law of Conservation of Energy.

The first man to find out an exact equivalence between the work done and the heat generated in the act of doing the work, was Joule. He showed that energy which disappears in overcoming friction etc., always re-appears as heat and is not lost, although it is rendered useless from the utility point of view. This brings into prominence the fact that *energy may change form, but is not destroyed*.

If, on giving an amount of heat dQ to a system, a work dW is obtained, then

$$dQ = dU + dW \quad \dots(i)$$

where dU represents the change in the *Internal Energy* of the system. This energy remains within the body and may have been used up in producing a change of temperature, or a change of state or in bringing about a change in the molecular spacing which occurs during expansion. The energy thus used up is called Internal Energy. The internal energy of a system depends upon its temperature, mass, volume, physical state, etc., and a change in any one or more of these quantities implies that a change in internal energy has taken place.

Equation (i) is the mathematical form of the **Law of Conservation of Energy**. The law states that 'in any inter-transformation of heat and molecular motion (or in any two types of energy) the amount of one form of energy which disappears is exactly equivalent to the amount of the other form which is created.'

For Joule the conservation law was not a mere speculation. It represents an inductive inference justified by a wealth of accurate data derived from a variety of accurate experiments, skilfully devised and patiently executed. He determined the work necessary to generate a unit amount of heat. In this venture, he was not satisfied by a single determination or even by a single series of experiments. He tried to produce heat in various ways and used various calorimetric substances. Not only this; he also showed that when heat is produced by an expenditure of electrical energy, the same amount of work must still be done to produce a unit quantity of heat.

The older physicists recognized *three* separate conservation laws for any isolated system—the laws of Conservation of Mass, Energy and Momentum. Einstein has introduced a new generalization by postulating the equivalence of mass and energy. According to Einstein, “*Every kind of energy, of any form whatever, represents a mass which is equivalent to this same energy divided by c^2 , where c is the velocity of light*” and further that, “*every quantity of energy in motion represents momentum*”. Mathematically expressed,

$$m = \frac{E}{c^2},$$

where m is the mass corresponding to an energy E . One gram of mass is equivalent to 9×10^{20} units of energy (in ergs).

6.2. Nature of Heat. According to Gassendi and other calorists, heat was a subtle, elastic, weightless, self-repellent fluid called **caloric** whose particles insinuated themselves into the interstices of matter and were held there by the attraction of the later. To explain differences in specific heats, it was postulated that caloric particles were attracted to the atoms of a substance with a force which varied with the heat capacity of the material. The particles of caloric were supposed to be in constant motion and repelling each other; this explained heat-flow. During a compression or rubbing, some of the caloric oozed out, producing a rise of temperature. The entry of caloric into a body resulted in a greater internal repulsion producing an increase in the size of the body. The temperature of the body did not rise during a change of state because the caloric formed a chemical compound with the substance. Solar radiation was simply a stream of caloric particles. Since the calorists were familiar with the fact that during a heat-transfer, the gain of heat always balances the loss, they postulated that *it was impossible to create or to destroy caloric*. The heat fluid had thus a great adaptability and any additional property could be given to it to meet any new situation!

In 1798, Rumford, an ordnance engineer at Munich, was surprised by the great evolution of heat, as the borer, turned round and round by the horses, worked its way into metal blocks in the act of boring cannon. The supply of heat seemed inexhaustible and given sufficient time any amount of heat could thus be produced. He argued that the production of heat was in some way connected with the movement of horses—the more they worked, the larger was the heat.

produced. Rumford remarked, "Anything which any insulated body, or system of bodies can continue to furnish without limitation, cannot possibly be a material substance, and it appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of anything, capable of being excited and communicated, in the manner the heat is excited or communicated, except it be MOTION".

It is thus clear that *the fluid theory cannot explain the production of heat by Friction*. Rumford's work created doubts in the minds of the scientific world about the true nature of heat and the scientists were set thinking furiously. It may not be beside the point to remark that much earlier, in the seventeenth century Bacon, Boyle, Newton, Hobbs and others had also put in the suggestion that the essence of heat was in some way to be found in Motion. But motion of what? The idea was never developed and the caloric theory reigned supreme for over a century.

Later, Davy obtained water by fastening two blocks of ice to a wooden rod each, and rubbing the blocks with each other in a closed space. The later precaution was taken to prevent the flow of heat to or from ice. Since each gram of water contains 80 calories of heat more than a gram of ice, heat has been created in this case. This gave a death-blow to the caloric theory.

6.3. Modern theory of Heat. According to Kinetic Theory, matter consists of molecules which are in incessant motion. On account of their close packing in solids, the molecules, though moving quite fast, generally cannot get away from their mean positions but merely oscillate about them. In liquids the binding forces are comparatively weaker and a molecule is free to move from one point in the liquid to another. In the case of gases the forces binding the molecules are negligible and a molecule can wander as it likes, though it very frequently comes into collision with its neighbours.

Heat, according to the present ideas, is nothing but the kinetic energy of the molecules of a substance. When heat enters a body, it increases the rate of molecular motion, *i.e.*, the to and fro movement of the molecules becomes more violent and tends to push the molecules apart—this explains why a body expands on heating. The increase in molecular movement also produces a rise in the temperature of the body. On the other hand, when heat is abstracted from a body, the molecular movement slows down, the body contracts in size and its temperature falls.

When one end of a solid is heated, the rapidly moving molecules at the hot end share their kinetic energy with their slower-moving neighbours by collisions and a flow of heat thus takes place in the direction of fall of temperature. During a change of state the heat supplied is used up in loosening the bonds between molecules and hence becomes latent (*i.e.* hidden) and does not produce a rise in the temperature of the body. Solar heat comes to the earth by Radiation—the rapidly oscillating molecules of the sun produce waves in the Ether (which is supposed to fill all space) and these waves carry the energy to the earth. When bodies on the earth absorb this

energy, their molecular kinetic energy increases and they show a rise in their temperatures.

The Modern theory of Heat is extremely simple, makes no *ad hoc* assumptions and is capable of explaining the diverse thermal phenomena. Its greatest merit lies in its simplicity.

6.4. Mechanical Equivalent of Heat. As a result of the classical experiments performed by him over a number of years, Joule stated that there is an exact equivalence between the amount of work over-come and the heat generated. He said that *no matter how work is done, if it be wholly spent in the production of heat, the same amount of work will always be necessary to produce a unit amount of heat.* No special method is indicated for doing the work. It may be spent in churning liquids, in hammering, in compressing a gas or may even be done electrically but always with the same result. In each case 4.2×10^7 ergs of work produce one calorie of heat. This is called the **Mechanical Equivalent of Heat** and is denoted by J .

6.5. Joule's experiment. To determine the amount of work necessary to produce one calorie of heat, Joule took a copper calorimeter having a number of copper vanes soldered to its sides. A spindle having similar vanes attached to it was placed centrally in the calorimeter. The

calorimeter was placed in a thick wooden case to protect it from heat losses.

The spindle carried a wooden cylinder R at its top. On fixing the pin P , the cylinder could be joined to the spindle but if the pin was removed the cylinder could rotate freely without rotating the spindle. A string carrying a weight M at one end was wrapped round the cylinder by turning the handle L , so that M stood near the pulley E . The calorimeter

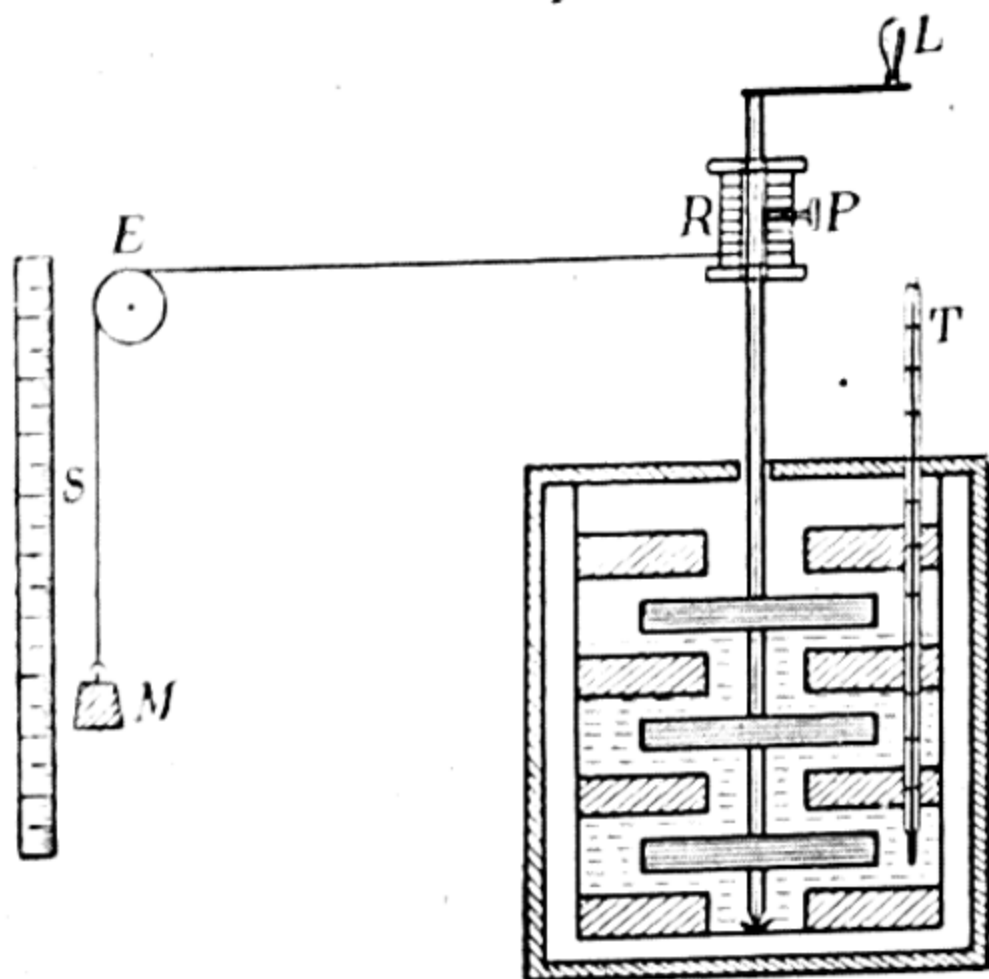


Fig. 6.1.
Joule's experiment.

contained a known weight of water whose temperature was given by the sensitive thermometer T . The pin was fixed and the weight was allowed to fall. As the spindle rotated, the water was churned but the movement of water was arrested by the fixed vanes. When M had reached the bottom, P was removed, the thread was re-wound on the cylinder, the pin was replaced and the weight allowed to fall again. This was repeated a number of times and the resultant temperature of the water noted.

If h be the height through which the weight falls n times, work done by the weight $= n.Mgh$ ergs. If m be the mass of water, w the

water—equivalent of the calorimeter and θ the rise of temperature, the heat produced $= (m + w)\theta$ calories.

$$J = \frac{W}{H} = \frac{n.Mgh}{(m + w)\theta} \text{ ergs/cal.}$$

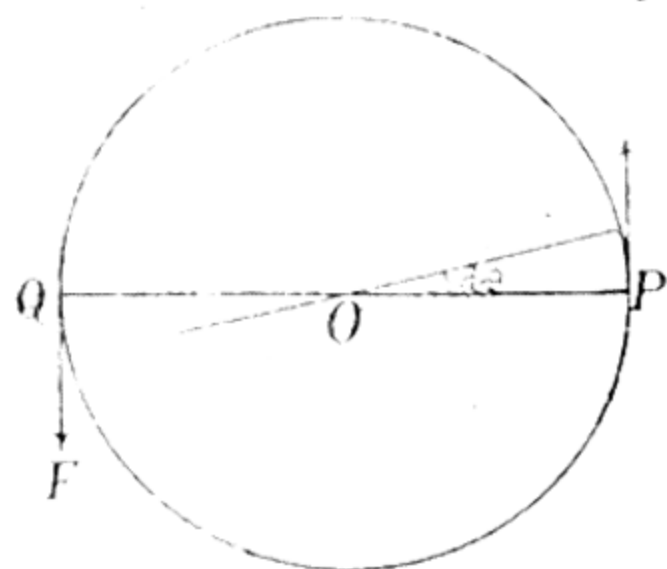
Joule repeated his experiments using various liquids in the calorimeter and also by changing the material of the calorimeters. His determinations gave $J = 4.2 \times 10^7$ ergs/cal.

The result is surprisingly correct although the rise of temperature was hardly half a degree per hour and although his thermometers had not been compared with any standard thermometer. To meet these objections the experiment was repeated by Rowland and others, with more refined and better apparatus.

6.6. In the words of Maxwell, Joule's law states that '*when work is transformed into heat or heat into work, the quantity of work is mechanically equivalent to the quantity of heat.*' This law is called the **First Law of Thermodynamics**; Thermodynamics is the science that deals with the conversion of mechanical work into heat and *vice versa*. It attempts at establishing an equivalence between the work done and the heat produced or to put it tersely 'Thermo-dynamics is the study of energy relationships and the direction in which the change occurs.'

Since work can be produced only by the expenditure of energy, in whatever form it may be, it follows directly from it that it is impossible to make a perpetual-motion-machine, *i.e.*, a device to obtain useful work continually without drawing on any energy-source. This fact was recognized by Newton, Stevinus and Leibnitz so far as its application to *purely mechanical engines* was concerned, but the discoveries of the nineteenth century showed that the principle applied to engines of all kinds.

6.7. Work done by a couple. Let the axis of rotation of a body acted upon by a couple pass through O and let a couple FF act perpendicularly at the ends of a diameter PQ .



Let the body rotate through an angle $d\theta$. The points P and Q will move through a distance $= OP.d\theta$. The work done by each force F is $F \times (OP.d\theta)$ and by the two together is $2 \times F \times (OP.d\theta)$

\therefore the work done by the couple in rotating the body through an angle θ is

Fig. 6.2
Work done by a couple.

$$W = \int_0^{\theta} 2F.OP.d\theta$$

$$= 2F.OP.\theta$$

= moment of couple \times angle of rotation or twist

[$\because F.2OP$ = moment of couple]

If the body makes n complete rotations, the angle $\theta = 2\pi.n$.

6.8. Rowland's Experiments. His apparatus consists essentially of a calorimeter having a set of vanes fixed to its sides and containing a weighed amount of water. A spindle with radial vanes projects into the calorimeter from below and can be rotated rapidly by means of a steam-engine whose shaft is attached to the spindle by means of a belt, as shown. The calorimeter is firmly attached to a stout metal rod AB (to which a wheel W is secured) and suspended by a strong torsion wire. A silk cord is wrapped round the wheel W and carries equal weights M, M , at its ends. The weights exert a couple tending to rotate the wheel and, therefore, the calorimeter also.

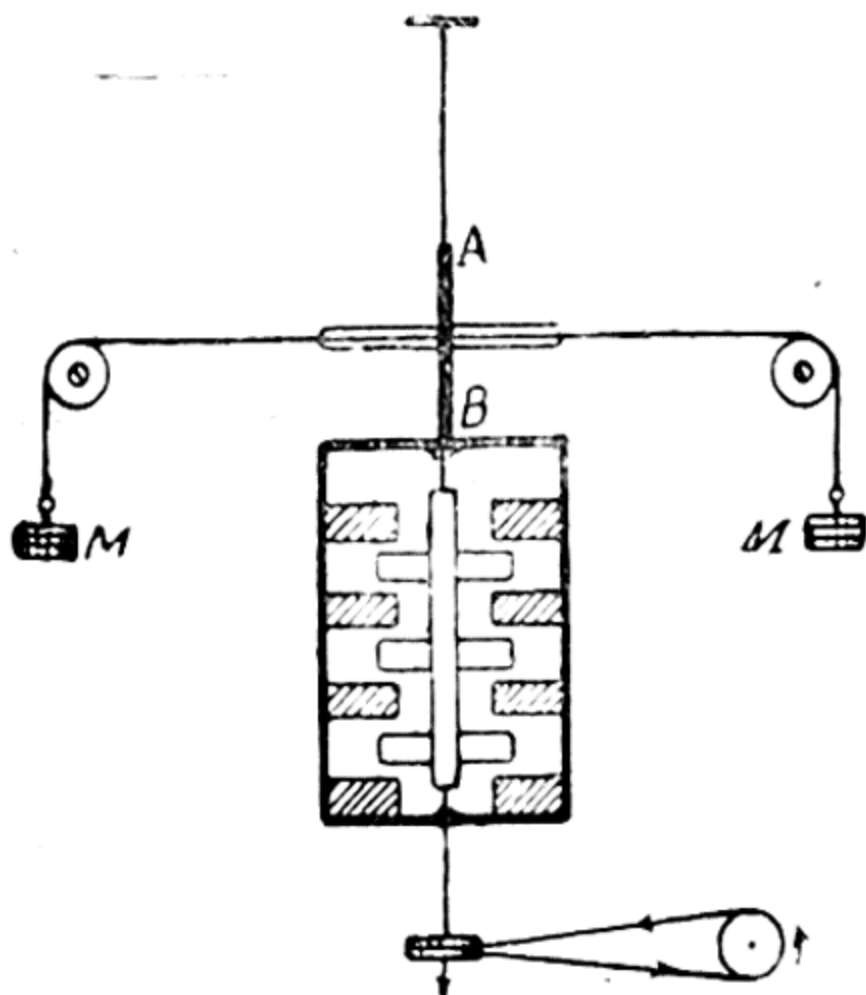


Fig. 6.3.
Rowland's apparatus for J .

The temperature of the water is recorded with a thermometer which has been compared with a standard hydrogen thermometer and the spindle is set rotating. The radial vanes set the water in motion which tends to rotate the calorimeter. The weights MM are so adjusted that they exert an equal and opposite couple on the calorimeter, which therefore remains in equilibrium. The friction between the rotating vanes and the water warms it up. Rowland obtained a rise of 35°C per hour in his experiments. The rotations of the spindle are automatically recorded by counters attached to it.

If w_1 be the weight of water and w_2 the water-equivalent of the calorimeter and t_1 and t_2 , the initial and final temperatures, the heat produced is $(w_1 + w_2)(t_2 - t_1)$ calories. The moment of the couple due to the weights $M, M = \text{either force} \times \text{perpendicular distance between the two forces} = Mg.d$ where d is the diameter of the wheel W . The work done by the spindle (whose moment is equal and opposite to that of MM) in n rotations is equal to, *couple \times angle of twist i.e., $Mgd. \times 2\pi n$ ergs.*

$$\therefore J = \frac{\text{Work done}}{\text{Heat produced}} = \frac{2\pi n.Mgd}{(w_1 + w_2)(t_2 - t_1)}$$

The radiation correction is calculated by allowing the calorimeter to cool with the paddles rotating slowly, just to keep the water stirred.

Rowland obtained the following values for J at various temperatures ;—

Temperature	Ergs needed to heat 1 gm. of water through 1°C
10°C	4.129×10^7
15°C	4.187×10^7
20°C	4.181×10^7
25°C	4.176×10^7
30°C	4.174×10^7

His value for J is 4.181×10^7 ergs per calorie at 20°C. The value of J was found by him to change slowly with temperature. This implies that the specific heat of water is not constant but changes with temperature. As already stated, the *calorie* is defined as the amount of heat necessary to raise the temperature of one gram of water from 14.5°C to 15.5°C. The *mean calorie* is $\frac{1}{100}$ of the heat required to raise one gm. of water from 0°C to 100°C.

6.9. Electric Method for J . This is due to Callender and Barnes. A *slow* stream of water flowing steadily through the narrow glass tube T is heated by an electric current (obtained from a standard cell) flowing through a thin wire of platinum placed centrally across it. The wire is secured at its ends to two thick copper tubes and platinum resistance thermometers T_1 and T_2 are

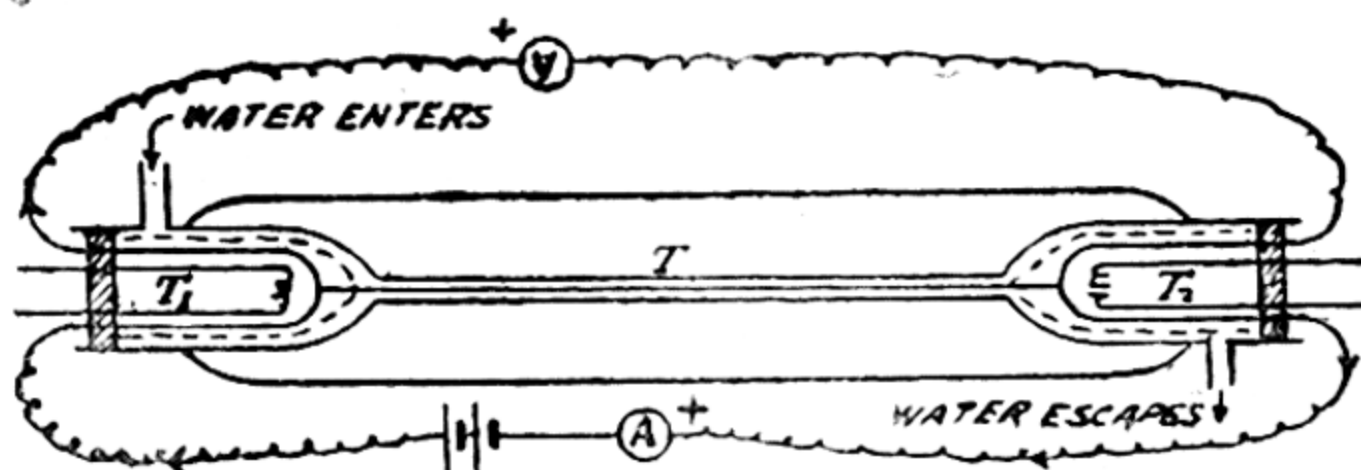


Fig. 6.4
Continuous flow method for J .

placed in these tubes which being good conductors at once communicate the temperature of the surrounding water to the enclosed thermometers. Moreover, since they have only a negligible resistance, they prevent the generation of any heat by the current in the immediate neighbourhood of the thermometer bulbs. The central glass tube is sealed into an outer glass jacket and the space between the two is exhausted to reduce heat losses to a minimum. The whole apparatus is immersed in a constant-temperature water-bath.

When the steady state has been reached both the thermometers are read. They give the initial and final temperatures, t_1 and t_2 , of water. The amount of water M flowing out in a certain time, t seconds, (as measured by an electric clock) is accurately weighed. The *P.D.* (E) at the ends of the wire and the current (I) flowing through it are measured by a sensitive voltmeter and ammeter respectively, which are joined to the copper tubes, as shown.

The heat gained by the water is $M(t_2 - t_1)$ calories and if H be the heat lost by radiation in the same time the total heat generated is $[M(t_2 - t_1) + H]$ calories. This is equivalent to $[M(t_2 - t_1) + H] \times J$ ergs. The energy of the current consumed is EIt watts $= E.I.t \times 10^7$ ergs (1 watt = 1 Joule/sec. = 10^7 ergs/sec.)

Hence $[M(t_2 - t_1) + H] \times J = E.I.t \times 10^7$ ergs.

To eliminate the radiation error H , the experiment is repeated after changing the rate of flow of water. It is, however, so arranged that the initial and final temperatures are the same as before. Since the rate of cooling is proportional to the excess of temperature of a body over its surroundings, the radiation error will be the same in both the cases. If M_1 , E_1 and I_1 are the values of M , E and I in the second case,

$$[M_1(t_2 - t_1) + H]J = E_1.I_1.t \times 10^7 \text{ ergs}$$

By subtraction H is eliminated and J can be found out. The value they obtained was $J = 4.1845 \times 10^7$ ergs at 15°C . This method possesses all the advantages of continuous flow calorimetry viz.,

- (1) The radiation losses are negligible.
- (2) Heat is produced electrically and can be measured with great exactness.
- (3) Temperatures being steady can be recorded with a greater precision.
- (4) The thermal capacity of the apparatus is eliminated when the steady state is reached.
- (5) The apparatus is very compact and the method of working is very neat.

The most accurate value of J determined by Jaeger and Steinwehr in 1921 is $J = 4.186 \times 10^7$ ergs at 15°C . They used a much larger quantity of water which was very efficiently stirred and they made use of a small rise of temperature (1.4°C) in order that Newton's Law of Cooling may be strictly applicable.

Example. In an experiment by continuous flow method, when the rate of flow of water was 11 gm. per minute, the heating current 2 amperes and P. D. between the ends of wire one volt, the rise of temperature of water was 2.5°C . On increasing the rate of flow to 25.4 gm. per minute, the heating current to 3 amperes and P.D. to 1.51 volts, the rise of temperature was still 2.5°C . Calculate the value of J .

(Punjab University)

(i) Case. Heat generated $= [11 \times 2.5 + H]J$ ergs/min.

Electric power consumed $= 1 \times 2 \times 60 \times 10^7$ ergs/min.

(ii) Case. Heat generated $= [25.4 \times 2.5 + H]J$ ergs/min.

Electric power consumed $= 1.51 \times 3 \times 60 \times 10^7$ ergs/min.

From (i) : $[11 \times 2.5 + H]J = 1 \times 2 \times 60 \times 10^7$

From (ii) : $[25.4 \times 2.5 + H]J = 1.51 \times 3 \times 60 \times 10^7$

By subtraction : $14.4 \times 2.5J = 2.53 \times 60 \times 10^7$

$$\therefore J = \frac{2.54 \times 60}{14.5 \times 2.5} \times 10^7 \text{ ergs/cal}$$

$$= 4.217 \times 10^7 \text{ ergs per calorie}$$

6.10. Variation of Sp. Heat of Water with Temperature.

It has already been stated that the value of J as determined by Rowland slowly changed with the initial temperature of water and that he was led to the conclusion that the specific heat of water was not the same at all temperatures. The set-up of his apparatus was, however, not suitable for the direct measurement of this variation of specific heat with temperature.

The apparatus of Callender and Barnes is very well-adapted for this determination. Water is made to flow through the apparatus at a *constant* rate but its initial temperature is changed in the various determinations. Thus the initial temperatures may be 10° , 20° , 30° etc., Electrical energy is supplied at the *same* constant rate in all the determinations. It is merely necessary to see that the readings of the ammeter and the voltmeter remain unchanged throughout the experiment. Then *the rise of temperature will be inversely proportional to the specific heats at the two temperatures*. Thus suppose that with 10°C as initial temperature, the rise in temperature of water is 8°C and at 20°C it is 8.5°C . Then clearly, a gram of water at 10°C requires more heat for a rise of temperature of 1°C than a gram of water at 20°C and the two quantities are in the ratio $8.5 : 8$. It is found that water possesses the minimum specific heat at 37°C . The values of the sp. heat at a few temperatures are :

Temperature	Sp. of Heat
10°C	1.0019
15°C	1.0000
20°C	0.9988
30°C	0.9976
35°C	0.9973
40°C	0.9973
50°C	0.9978
70°C	1.0000

The curve depicting the variation in the specific heat of water with temperature is shown below.

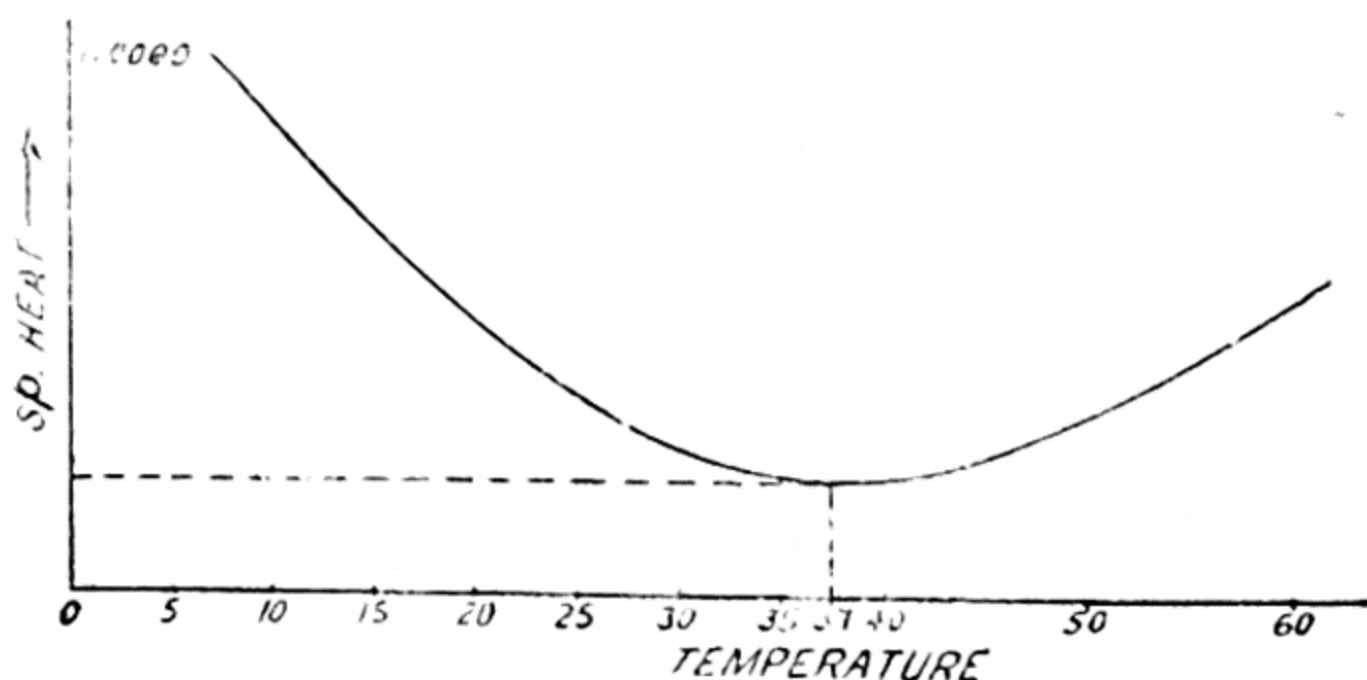


Fig. 6.5

Curve showing change of sp. heat of water with temperature

6.11. J. from Sp. Heats of a Gas. The sp. heat of a gas at constant pressure is greater than the sp. heat at constant volume by an amount equal to the heat-equivalent of the external work done. Meyer calculated J from the above consideration of the sp. heats of a gas.

The heat required to heat up one gm. of a gas at constant pressure through dT° is $1.C_p.dT$, and that at constant volume $1.C_v.dT$. In the former case, heat is absorbed by the gas not only for a rise of temperature (as in the second case) but also for doing work in expanding against external pressure. If p be the pressure and dv the increase in volume, the external work done is $p.dv$.

$$\therefore 1.C_p.dT = 1.C_v.dT + \frac{p.dv}{J}, \quad \dots \dots (i)$$

expressing $p.dv$ in heat units.

Also, since a gas obeys Boyle's law

$$pv = rT$$

or

$$p.dv = r.dT, \text{ since } p \text{ is constant.}$$

Putting this value of $p.dv$ in (i) we have

$$C_p.dT = C_v.dT + \frac{r.dT}{J}$$

or

$$C_p = C_v + \frac{r}{J}$$

or

$$C_p - C_v = \frac{r}{J} \quad \dots \dots \dots (ii)$$

Knowing C_p , C_v and r , J is at once found out.

If $p.dv$ is being measured in heat units, J is omitted and (ii) is written in the form

$$C_p - C_v = r \quad \dots \dots \dots (iii)$$

If C_p and C_v are the sp. heats per gram-molecule of the gas (and not per gm. of the gas as above), (iii) is written in the form

$$C_p - C_v = R \quad \dots \dots \dots (iv)$$

Example 1. Calculate sp. heat at constant volume for air, given that its sp. heat at constant pressure is 0.23 . $J = 4.2 \times 10^7$ ergs and density of air = 1.3 gm./litre at N.T.P.

Since sp. heat per gm.-mol. is not given, use (iii)

$$C_p - C_v = \frac{r}{J}$$

or

$$C_v = C_p - \frac{r}{J} \quad \dots \dots \dots (1)$$

To calculate r , use the relation $p.v = r.T$, where v is the volume of one gm. of air.

$$\therefore (76 \times 13.6 \times 981) \times \frac{1000}{1.3} = r.273.2$$

or

$$r = \frac{76 \times 13.6 \times 981 \times 1000}{1.3 \times 273.2} = 0.28 \times 10^7 \quad (2)$$

Substituting in (1) $C_v = .23 - \frac{.28 \times 10^7}{4.2 \times 10^7}$
 $= .23 - .07$
 $= .16.$

Example 2. Calculate the sp. heat at constant volume for hydrogen given that its sp. heat at constant pressure is 6.85 calories per gm. mol. Density of hydrogen at N.T.P. = .0899 gm./litre and $J = 4.19 \times 10^7$ ergs./calorie.

$$C_p - C_v = \frac{R}{J}.$$

$$\therefore C_v = C_p - \frac{R}{J} = 6.85 - \frac{R}{J} \quad \dots(i)$$

To get R , we have $pv = R.T$ where v is the gram-molecular volume i.e., the volume occupied by 2.016 gm. of hydrogen.

$$\therefore (76 \times 13.6 \times 981) \times \left(\frac{1000}{.0899} \times 2.016 \right) = R \times 273.2$$

$$\therefore R = 8.31 \times 10^7 \text{ ergs.}$$

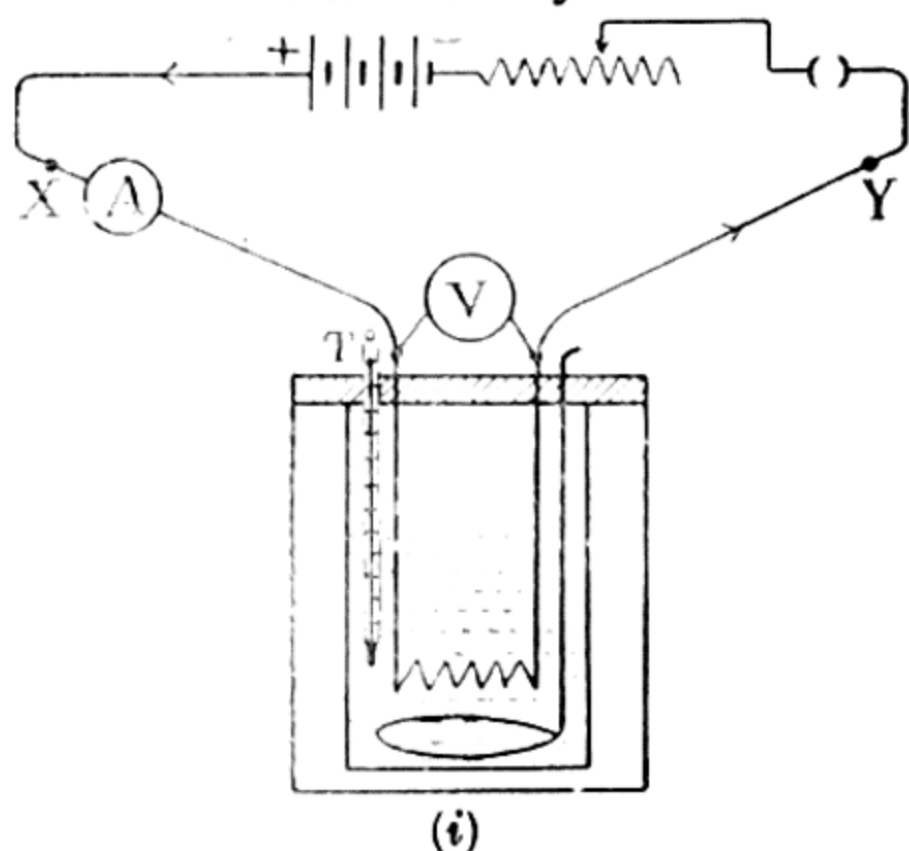
From (i)

$$C_v = 6.85 - \frac{8.31 \times 10^7}{4.19 \times 10^7}$$

$$= 6.85 - 1.986$$

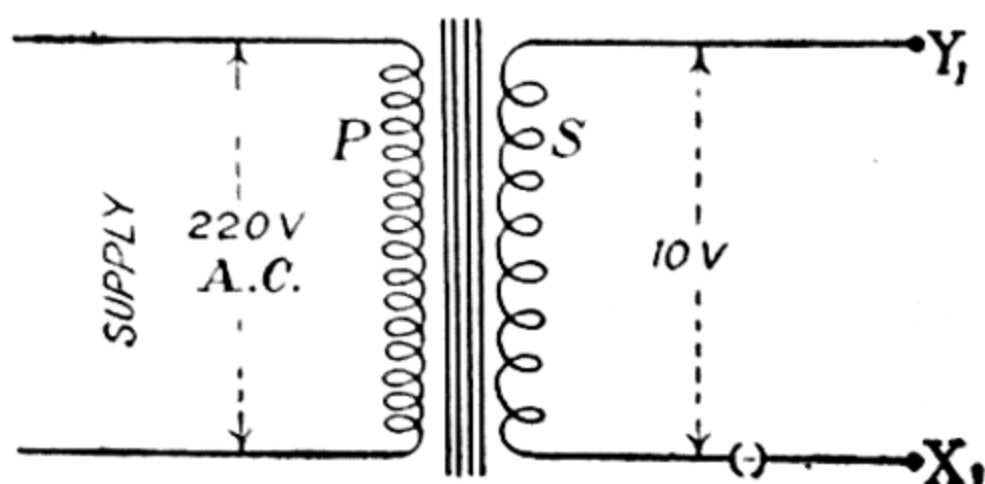
$$= 4.864 \text{ cal. per gm. mol.}$$

6.12. Laboratory Method for J.



Water contained in a jacketed calorimeter is heated by a low-resistance heating coil through which a current of about 2 amperes at 8–10 volts is passed for 10 minutes so that a rise of about 8°C is produced, the rise of temperature being noted after thorough stirring. The current is now switched off and the calorimeter and its contents are allowed to cool for ten minutes. Half the drop in temperature is added to the final temperature to allow for radiation losses.

When working with direct currents, the current is reduced to a suitable value with a rheostat [fig (i).] When working with A.C. the current is lowered in voltage by using a step-down transformer, whose primary coil P is joined to the supply while the points X_1 and Y_1 of the secondary are joined to X



(ii)
Laboratory method for J,

and Y in [fig (i)] and A.C. voltmeter and ammeter are used for measurements of P. D. and current.

The heat gained by the water and calorimeter is

$$H = (m + w)(\theta_2 - \theta_1) \text{ calories}$$

and the work done electrically is $W = E.I.t \times 10^7$ ergs, whence

$$J = \frac{W}{H} = \frac{E.I.t \times 10^7}{(m + w)(\theta_2 - \theta_1)}$$

where the symbols have their usual meaning.

*Example :—*A current of 2 amperes at 10 volts is passed through a calorimeter of water-equivalent 5 gm. containing 400 gm. of water, for 9 minutes and a rise of temperature of 6°C is observed. When the calorimeter is now allowed to cool for 9 minutes the temperature falls by 0.5°C . Determine J .

$$\text{Corrected rise of temperature of water} = 6 + \frac{0.5}{2} = 6.25^\circ\text{C}.$$

$$\text{Heat gained by water} = (400 + 5) \times 6.25 \text{ cal.}$$

$$\text{Heat produced electrically} = 10 \times 2 \times (9 \times 60) \times 10^7 \text{ ergs.}$$

$$\therefore J = \frac{10 \times 2 \times 9 \times 60 \times 10^7}{405 \times 6.25} \\ = 4.27 \times 10^7 \text{ erg/cal.}$$

6.13. Jaeger and Steinwehr's method (1921). These workers used a thin calorimeter (weight 0.45 kgm.) so that its thermal capacity was insignificant as compared with that of 50 kgm. of water contained in it, and therefore it was not necessary to determine the former with any great accuracy. A large quantity of water was taken to reduce loss of heat by radiation (because increase in surface-area is proportionately much smaller than any increase in volume). Water was heated electrically by passing a weak current (whose amperage and voltage was determined very accurately) through a low-resistance heating coil C and the rise of temperature which was only 1.4°C (so that Newton's law of cooling may be strictly applicable when deter-

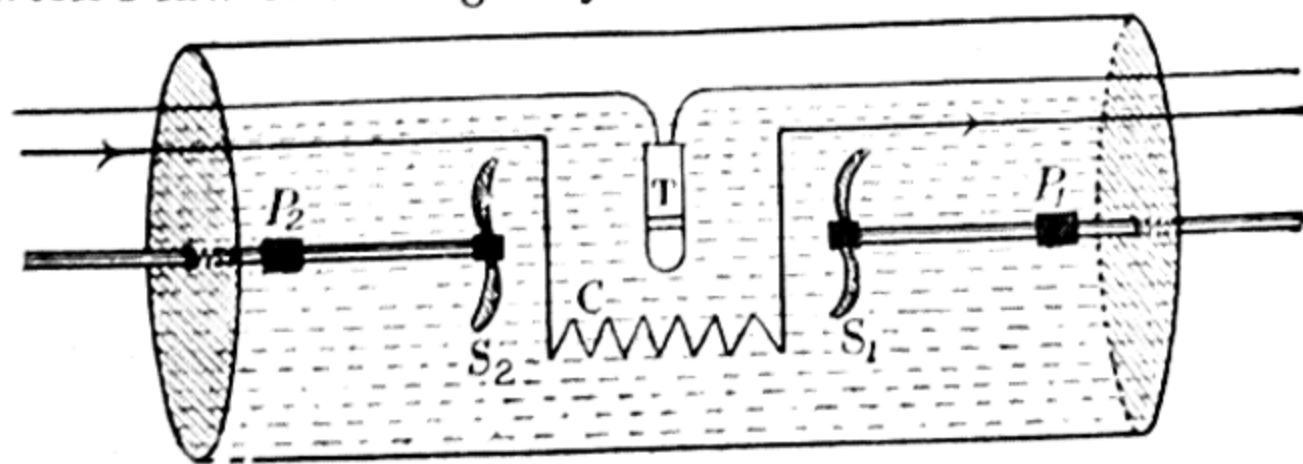


Fig 6.7

Jaeger and Steinwehr's method for J .

mining radiation losses) was measured by a Platinum resistance thermometer T . The calorimeter was placed with its axis horizontal in a double-walled jacket through which water at practically the same temperature as that in the calorimeter, was circulated. The water was stirred efficiently with the electric stirrers S_1, S_2 mounted on a horizontal shaft which had its parts P_1, P_2 made of vulcanite to prevent

conduction of heat to the outside along the shaft. J was calculated in the usual manner. Their determination gives

$$J = 4.186 \times 10^7 \text{ ergs/calorie.}$$

6.14. Zero-th law of Thermodynamics. There are four laws of thermodynamics. The first law has been discussed in this chapter. The second law is dealt with in chapter XII. The third law is also briefly referred to in the same chapter.

The **zero-th law** states that, '*Two bodies or systems in thermal equilibrium with a third are in thermal equilibrium with each other*'.

It follows from this that an isolated system tends, with time, towards an equilibrium condition with a constant temperature throughout. By an isolated system we mean a system, that does not receive energy from or transmit energy to other bodies or systems. Such a system cannot be realized in practice because no system can be perfectly shielded from gaining or losing any heat whatsoever. We can, however, approximate very closely to such an ideal system.

If two liquids A and B , at different temperatures, are mixed in a calorimeter (which has been thermally insulated, as much as possible, from its surroundings) and if a thermometer be placed in the calorimeter, we can consider A , B , calorimeter and thermometer as an isolated system. Given time, the four will reach a state in which all of them have a common temperature and are in thermal equilibrium. Any pair, out of the four, will also be in thermal equilibrium; which is the zero-th law.

QUESTIONS

1. Give the Rowland's method for determining J . What are its merits over Joule's arrangement?

2. What is mechanical equivalent of heat? Explain with a clear sketch Callendar and Barnes' method for determining J . What are the chief merits of continuous flow calorimetry?

3. Obtain an expression for the difference between the two principal sp. heats of a gas in terms of other measurable quantities.

4. Calculate C_p for air, given $C_p = .23$, Density of air at 27°C , and standard pressure = $1.18 \text{ gm. per litre}$, $J = 4.2 \times 10^7 \text{ ergs}$.

[Hint. $T = (273 + 27)$.]

5. Calculate the difference between the two principal sp. heats of hydrogen, given that $1 \text{ gm. of hydrogen occupies } 11.2 \text{ litres at N.T.P. and } J = 4.2 \times 10^7 \text{ ergs./calorie}$. [Ans. $.99 \text{ cal.}$]

6. Calculate J from the following data.

In the continuous flow method, when the rate of flow of water was 30 gm./min. current two amperes and P. D. 3 volts, the rise of temperature was 2.7°C . When the flow was increased to 48 gm. , current to 2.5 amp. and P. D. to 3.75 volts. , the rise of temperature was still 2.7°C .

[Ans. $4.165 \times 10^7 \text{ ergs.}$]

7. Water oozes out from a porous pot, the pressure inside being 20 atmospheres more than that outside. If the temperature of water inside be 10°C what will it be on coming out? $J = 4.2 \times 10^7 \text{ ergs./cal.}$ Atmospheric pressure = $1.05 \times 10^6 \text{ dynes/sq. cm.}$

[Suppose $m \text{ gms. of water ooze out of one sq. cm. area of surface. } m \text{ gm. occupy } m \text{ c.c. Since area of surface} = 1 \text{ sq. cm., the length of the column of water coming out} = m \text{ cm. i.e., water moves through a distance of } m \text{ cm.}$

Work done *by* the difference of pressure is
 $(76 \times 13.6 \times 981) \times 20 \times m$ ergs

$$\therefore \text{Equivalent amount of heat lost} \\ = \frac{(1.05 \times 10^6) \times 20 \times m}{4.2 \times 10^7} \text{ calories} \\ = 0.5 m \text{ calories.}$$

If fall of temperature be $t^\circ\text{C}$

$$m \times t = 0.5m \text{ or } t = 0.5^\circ\text{C.}$$

$$\therefore \text{Outside temperature} = 10 - 0.5 = 9.5^\circ\text{C}]$$

8. What do you understand by the Internal energy of a system.

Write a note on the principle of conservation of energy.

9. Write an essay on the nature of heat, explaining therein what facts led to the downfall of the Caloric Theory.

10. Explain the modern theory of Heat. How does it account for the various thermal phenomena. What are the chief merits of this theory.

11. State the First law of Thermodynamics. Give an account of Joule's determination of the mechanical equivalent of heat. What were the weak points in his determination and how were they corrected by Rowland.

12. Does the specific heat of water change with temperature. How can this be tested experimentally.

13. Describe a simple laboratory method for determining J and give the necessary calculations.

14. Describe the method of Jaeger and Steinwehr for determining J. What is the chief merit of their determination.

CHAPTER VII

KINETIC THEORY OF GASES

Matter can be compared to a large flock of sheep on a hillside, which from a distance appears as a stationary white patch even though the individual sheep are moving and the lambs are skipping.—*Lucretius*.

Our theories consist fundamentally in the setting up of a model which has properties analogous to the phenomena which we have observed.—*E. Langmuir*.

7.1. Kinetic Theory of gases. According to kinetic theory, a gas is a congregation of an enormous number of extremely small particles called **Molecules**. These molecules rush about through comparatively large empty spaces (with velocities of the order of a mile per second at ordinary temperatures) and frequently come into collision with other molecules. The path of a molecule is an irregular

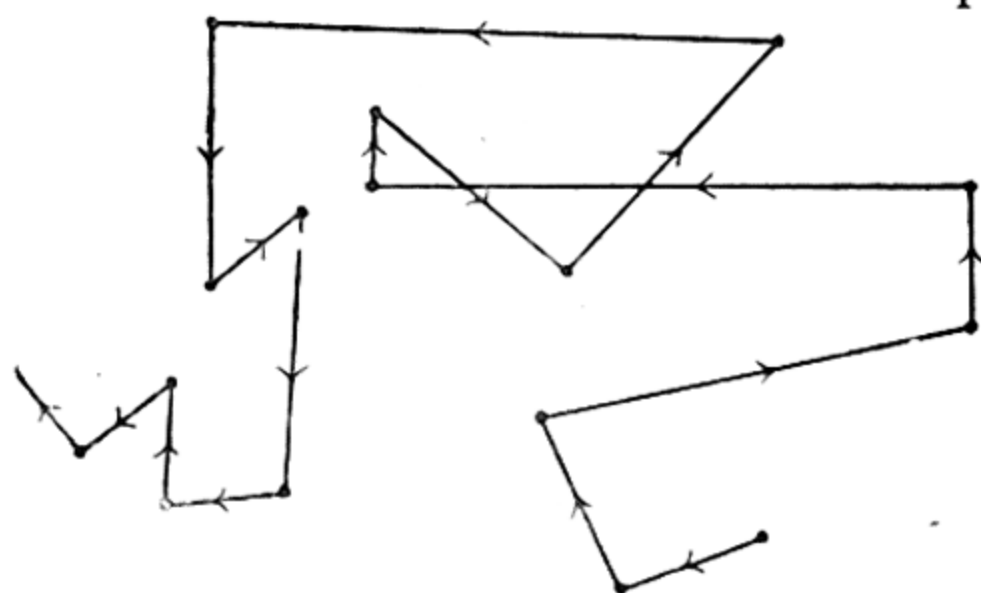


Fig. 7.1
Path of a molecule.

zig-zag having at each corner a collision with another molecule and consisting of straight paths between two collisions. The individual lengths of these paths vary widely, but the average for a large number of such paths has a definite value at any one temperature and is called the **Mean Free Path**. For air at N. T. P. it is about nine times the molecular diameter.

A molecule travels undisturbed in a straight line until it comes very close to another molecule when it is abruptly deflected due to the influence of the latter. Usually the molecule undergoes a change of speed also. Such a meeting is called an **Encounter** and is of an extremely short duration. No matter what velocities the molecules in a sample of gas possessed initially, their repeated encounters with one another will quickly destroy any uniformity that may have existed initially and a perfect *molecular chaos* will prevail. The velocities of the molecules and their directions of motion are distributed entirely at random. In such a state of molecular chaos, the number of molecules possessing velocities between say, u and $u+du$, at any temperature, remains sensibly the same and is not affected by the repeated encounters between molecules. If the velocities of some molecules are increased by those encounters, an equal number will suffer an identical decrease in their velocities. This is so, because the number of molecules involved is tremen-

dously large, e.g., the number of molecules in one cubic centimeter of a gas at N.T.P is 2.7×10^{19} .

We may therefore assert that *all the molecules in any sample of a gas, though moving with widely different speeds have a certain average speed which remains constant as long as the temperature does not change.* They also possess a certain average kinetic energy. With a rise in temperature both the molecular movement, and molecular kinetic energy increase.

Maxwell has calculated that at any given temperature, the largest percentage of molecules in any sample of gas have a velocity

$$= \sqrt{\frac{2kT}{m}}, \text{ represented by } OM \text{ and as shown by the graph, a vast}$$

majority of all the molecules, have velocities which do not differ widely from this mean. The r. m. s. velocity of the

$$\text{molecules (art. 7.6)} = \sqrt{\frac{3kT}{m}}$$

The percentage of molecules having velocities very much in excess or very much in defect of this average is very small indeed. Thus, although we are not able to say what the velocity of any individual molecule, selected at random is, we can give a measure of

of the average velocity of all the molecules in a sample of the gas, as also the percentage of molecules having a velocity lying between any limits, say, between u and $u+du$. Thus out of n molecules per c.c, the number dn having velocities lying between u and $u+du$

$$\text{is given by } dn = 4\pi na^3 \cdot e^{-bu} u^2 du. \text{ where } a = \sqrt{\frac{b}{\pi}} = \sqrt{\frac{m}{2\pi kT}},$$

where m = mass of one molecule, k = Boltzman's constant and T = absolute temperature.

Boltzmann has shown that the Maxwellian distribution is the only steady distribution and further that any other distribution would almost certainly be altered by collisions in such a way as to approach the Maxwellian form.

With a rise of temperature, the point M will move to the right i.e., velocities of molecules will increase with increasing temperature.

7.2. Experimental test of Maxwell's Law of Velocity distribution. In an arrangement due to Hall, Zartman and Ko, Bismuth vapour is allowed to stream out through a narrow slit S_1 in an oven which is heated uniformly on the outside. A narrow parallel beam is selected by putting another slit S_2 parallel to S_1 and at some distance from it. A drum D , having a narrow slit S at one side and capable of rapid rotation in the direction of the arrow is adjusted above S . A

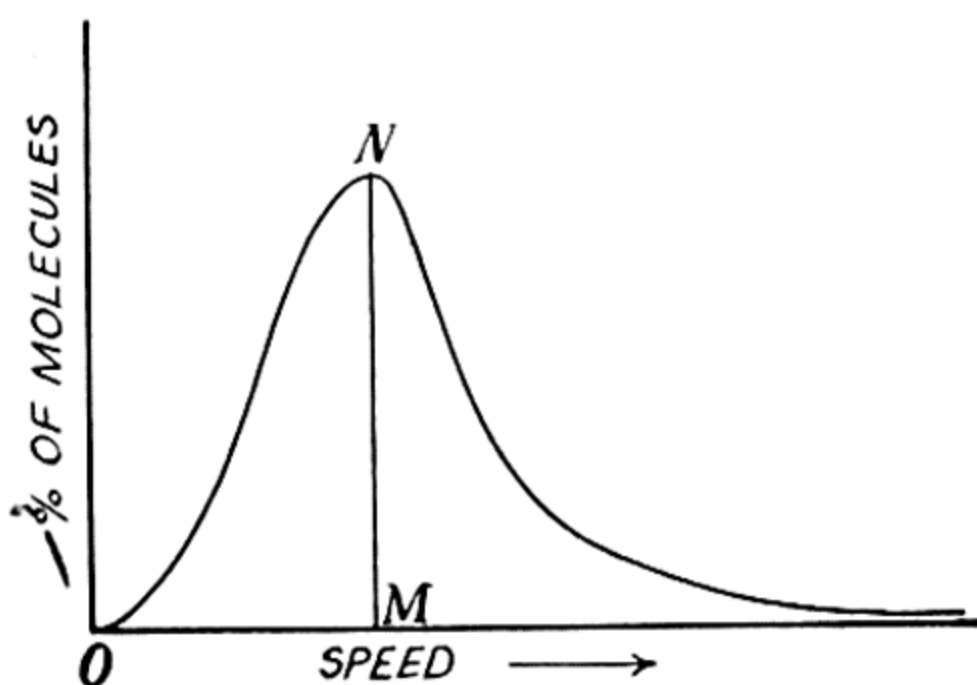


Fig. 7.2
Maxwell's distribution of molecular speeds.

glass plate P is placed at the back of D on the inside, opposite S .

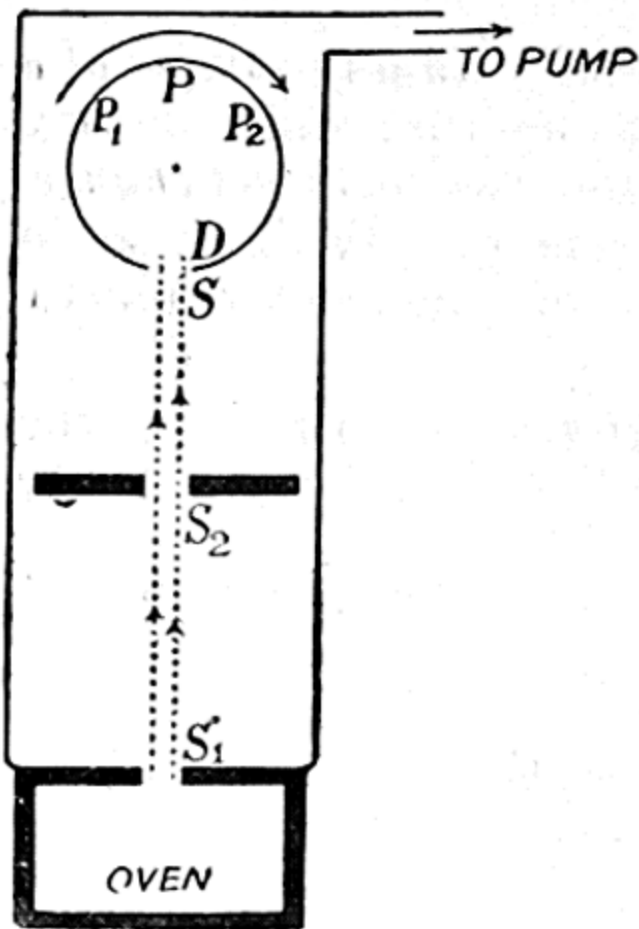


Fig. 7.3.
Zartman's experiment.

The molecular beam falls for the most part of the rotation on the outside of the drum except when S face S_2 . The beam then enters the drum (*The entire path of the beam, outside the oven, lies in a high vacuum*). By the time, the molecular beam entering at S is able to reach P , the drum has rotated through a small angle. The slowest molecules will take the largest time and will be deposited at P_1 while the fastest will go to P_2 . To condense the molecules the plate P is cooled on the outside with liquid air, if necessary. The thickness of the deposit at any point on P varies with the molecular speed. A velocity spectrum is thus obtained, and this amply corroborates the Maxwellian distribution of velocities (Fig. 7.2).

Gas	r. m. s. velocity at 0°C cm/sec	Mean free path at N. T. P. cm	Molecular diameter cm.
Hydrogen	18.39×10^4	18.3×10^{-6}	2.17×10^{-8}
Helium	13.11	28.5	1.92
Nitrogen	4.93	9.44	2.95
Oxygen	4.61	9.95	2.7
Carbon-di-oxide	3.92	6.29	2.9

7.3. Slowness of gaseous diffusion. A question was asked in the early days of the kinetic theory that if molecules really move about so fast, two gases ought to mix with some rapidity. Clausius's reply was that the progress of molecules from point to point is not an un-interrupted flow through the rest of the gas. There is a continuous interference by the molecules with each other's motion. If chlorine gas be released in one corner of a room, its odour is perceived in the opposite corner after some time, may be after a few minutes. Now a molecule of chlorine covers one-quarter mile per second, but this long path is converted into a complicated zig-zag by collisions with other molecules and is thereby twisted into a space of less than one square inch in area.

7.4. Gas pressure. A characteristic property of a gas is its tendency to expand indefinitely. Its molecules continually strike against the walls of the containing vessel and by their impact exert a

pressure on its walls. If the space available to the molecules be decreased, they will strike the walls of the container more often because although their kinetic energy is unaltered, the space available to them for movement has decreased and the gas will exert a greater pressure.

Again, when a gas is compressed, its temperature also rises. Thus if a piston moves into a cylinder of gas, the velocity of rebound of the molecules from the moving piston will be increased *i.e.*, their kinetic energy will increase or a rise of temperature will result. If the gas be allowed to expand by withdrawing the piston, the velocity of rebound of the molecules from the retreating piston will decrease; this means the molecular kinetic energy will decrease resulting in a fall of temperature.

7.5. Liquid and Solid States. If a gas under a *suitable* pressure be steadily cooled, the average kinetic energy of its molecules will go on decreasing and it will ultimately liquefy. It is, therefore, clear that the average kinetic energy of liquid molecules is less than that of molecules in the gaseous state. The erratic molecular movement is still there though it is on a much restricted scale due to their much closer packing. The **Brownian movement** (1828) is a visible evidence of the eternal dance of the liquid molecules. Very minute particles, *e.g.* pollen seeds, suspended in water appear to possess an eternal unceasing motion when viewed under a powerful microscope. This movement appears neither to stop nor slow down. The motion is independent of the nature of the suspended particles and is determined only by their size. The particles are pushed this way and that by the impact of the liquid molecules and show an erratic behaviour. The particles are in thermal kinetic equilibrium with the liquid molecules and have the same kinetic energy but as their mass is larger they move at a much slower rate. In any case they reveal the pattern of molecular motion in liquids.

Due to the closer packing of the molecules, the freedom of molecular movement is on a very much restricted scale in liquids. In liquids the molecules exert considerable attractive influence on one another and a molecule of a liquid cannot escape because of the backward pull of the other molecules. When however a liquid is heated, the K.E. of its molecules increases, and a molecule, moving at a rapid rate, may tear itself off and lead on independent existence. This is *evaporation*. If during its random motion, the molecule comes close to the liquid surface, it will be attracted into it again. This is *condensation*. When evaporation goes on in a closed space, some of the molecules leaving the liquid also return to it. When the space becomes fully saturated, the molecules leaving the liquid are balanced by those entering it. This exchange goes on continuously and the equilibrium is *dynamic*.

In a solid, the molecules are packed very closely together, so that although their motion is rapid, it is an oscillation about an average position. It may be likened to that of a man in a crowd where it is almost impossible for him to leave the space he occupies

between his neighbours. Yet he may turn round and have some slight motion from side to side. It is the great attractive force between neighbouring molecules which makes it so difficult for a solid to change its shape. In a liquid, the molecules are usually less closely packed and the forces binding molecules together are also weaker. The molecules are sufficiently free to move within the liquid-mass from one point to another. Their movement is like that of a man moving in a crowded street. He is pushed this way and that but can ultimately manage to escape.

It is not always true that the molecular spacing is larger in the case of liquids as compared to solids ; it may in fact be smaller—*e.g.* ice contracts on melting. What is important is a difference in the type of motion. A change in the position of the whole molecule as compared with a mere oscillation about a mean position shows the essential difference in nature between the liquid and solid states. When a change of state takes place the molecules themselves are unaltered. It is merely their organization that has been changed.

Again it is a well known experimental fact that the latent heat of fusion is much smaller than the latent heat of vaporisation. Thus their values for sodium, lead, and mercury are 630, 1170, 560 ; and 23,300, 46,000 and 14,200 calories/ gm. respectively. The latter are 30 to 40 times larger than the former. This means that *the binding forces between molecules decrease comparatively very slightly during fusion*. Specific heats are also very little affected by fusion.

Solids and liquids appear incompressible, not because their volume is actually full of matter, but because the forces between molecules hold them apart and also prevent other molecules from slipping in. "A number of soldiers with fire-arms may occupy an extensive region to the exclusion of the enemy's armies though the space filled by their bodies is small," that is how Maxwell describes the whole situation so very graphically.

7.6. Pressure exerted by an Ideal Gas. We have already noticed that the pressure exerted by a gas is due to the bombardment of the sides of containing vessel by the rapidly moving molecules. In deducing an expression for the pressure exerted by an ideal gas *i.e.*, by a gas rigorously obeying the relation $PV=RT$, it is assumed that—

(1) The size of the molecules is negligible and that they are so far apart from one another that their mutual attractions are nil.

(2) The encounters of the molecules with one another and with the walls of the vessel are perfectly elastic and entail no loss of energy.

(3) The time for which an encounter lasts is negligible as compared with that spent in moving freely.

(4) Between two collisions a molecule moves in a straight line with a uniform velocity.

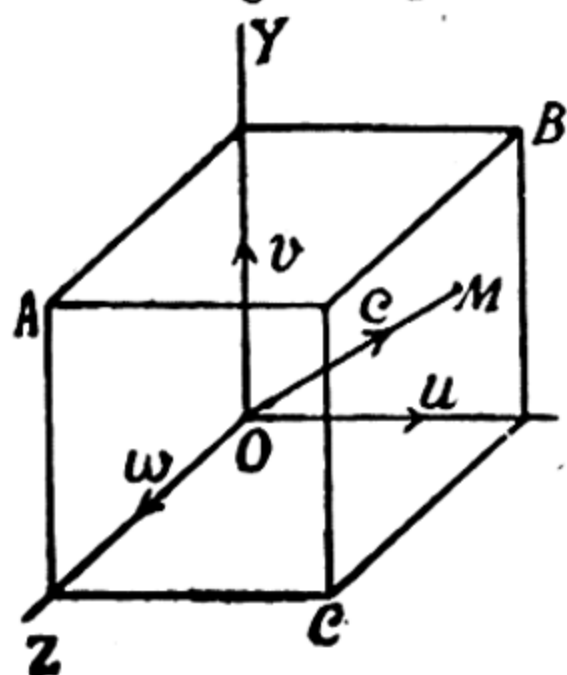


Fig. 7.4

To illustrate gas-pressure

Imagine a perfect gas enclosed in a cubical vessel of *unit* side, with the axes of co-ordinates parallel to its three sides. Let OM represent the velocity c of a molecule M . It can be resolved into components u, v, w parallel respectively to the three axes OX, OY and OZ , such that

$$c^2 = u^2 + v^2 + w^2.$$

A molecule of mass m moving with a velocity u along OX will experience a reversal of velocity after an elastic collision with the face BC . The change in its momentum will be $mu - (-mu) = 2mu$. It will strike the face BC $u/2$ times in one second and the total change in its momentum per second will be $2mu \cdot u/2$

$= m \cdot u^2$. Since pressure is equal to change of momentum per second for unit area of a surface, the total pressure exerted on the face BC by all the molecules will be

$$p_1 = m(u_1^2 + u_2^2 + u_3^2 + \dots + u_n^2) = m \cdot n \cdot \overline{u^2},$$

where $\overline{u^2}$ is the mean square velocity of all the molecules, n in number.

Similarly the pressure on the other two faces will be

$$p_2 = mn\overline{v^2} \text{ and } p_3 = mn\overline{w^2}.$$

But the pressure exerted on each face is found, by experiment, to be the same. Hence $p_1 = p_2 = p_3 = p$.

$$\therefore p = \frac{1}{3} (p_1 + p_2 + p_3) = \frac{1}{3} mn (\overline{u^2} + \overline{v^2} + \overline{w^2}) = \frac{1}{3} mn \overline{c^2}$$

where $\overline{c^2}$ is the resultant mean sq. velocity.

It can be put in the form

$$p = \frac{1}{3} mn C^2.$$

C is known as the root mean square velocity.

$$\text{Again } p = \frac{2}{3} n \left(\frac{1}{2} m c^2 \right).$$

or the pressure exerted by an ideal gas is equal to two-thirds of the kinetic energy of all the molecules contained in a unit volume of the gas.

Since the density ρ of the gas is equal to the mass of all the molecules contained in a unit volume of the gas,

$$\rho = mn$$

$$\therefore p = \frac{1}{3} \rho \cdot C^2 \text{ or } \frac{p}{\rho} = \frac{1}{3} C^2$$

Since C is constant if temperature does not change, $\frac{p}{\rho}$ is also constant under the same conditions. This is Boyle's Law.

Since $\rho \propto \frac{1}{V}$, we have $pV = \text{constant}$, which is the usual form of Boyle's law.

7.7. Calculation of Molecular Velocities. (1) The root mean-

square (*r.m.s*) velocity of the gas molecules can be calculated from the relation

$$p = \frac{1}{3} \rho C^2$$

$$C = \sqrt{\frac{3P}{\rho}}$$

Example. Calculate the *r.m.s.* velocity of nitrogen molecules at 0°C , given density of nitrogen at N.T.P. is $\cdot 00125$ gm./c.c.

$$C = \sqrt{\frac{3 \times 76 \times 13.6 \times 981}{\cdot 00125}}$$

$$= 4.93 \times 10^4 \text{ cm./sec.}$$

(2) If M be the molecular weight of a gas and V the gram-molecular volume,

$$\rho = \frac{M}{V}$$

$$\therefore p = \frac{1}{3} \cdot \frac{M}{V} C^2 \text{ or } pV = \frac{1}{3} MC^2$$

also

$$pV = RT$$

$$\therefore \frac{1}{3} MC^2 = RT \text{ or } \frac{1}{2} MC^2 = \frac{3}{2} RT. \quad \dots (i)$$

and

$$C = \sqrt{\frac{3RT}{M}}$$

Also $M = m.N$ where m is the mass of one molecule and N the Avogadro number *i.e.*, the number of molecules in a gram-molecule of the gas $= 6.06 \times 10^{23}$

Substituting in (i)

$$\frac{1}{2} mNC^2 = \frac{3}{2} RT$$

$$\frac{1}{2} mC^2 = \frac{3}{2} \cdot \frac{R}{N} \cdot T$$

$$= \frac{3}{2} k.T.$$

where $k = R/N$ is called Boltzmann's constant $k = 1.4 \times 10^{-16}$ ergs/degree

Hence the mean kinetic energy of translation of one molecule is $\frac{3}{2} kT$, whatever the mass of the individual molecule. The mean kinetic energy of the molecules of all gases is the same at the same temperature. It easily follows that the mean square speed of oxygen molecules is one-sixteenth of that of the hydrogen molecule.

Example (i) Calculate the *r. m. s.* velocity of hydrogen molecules at N.T.P.

$$\frac{1}{2} MC^2 = \frac{3}{2} RT$$

$$\text{or } C = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.31 \times 10^7 \times 273}{2.016}} = 1.84 \times 10^5 \text{ cm./sec.}$$

or well over a mile per second. The mean free path is only 1.8×10^{-5} cm.

The molecular speeds are surprisingly large. This means that our bodies are continually being bombarded by molecules moving with the speed of rifle-bullets without our becoming in the least conscious of it. But there is nothing surprising about it because the body is used to it.

A sound wave in a gas is propagated by the movement of its molecules and so the speed of sound waves cannot be greater than the mean speed of the molecules. Thus, the speed of sound in air at N.T.P. is 332 metres per second and is two-thirds of the speed of nitrogen molecules.

Example (ii) Calculate the kinetic energy of the molecules of one gram of Helium at 0°C

We know that the K.E. of M gm. is

$$\frac{1}{2} MC^2 = \frac{3}{2} RT$$

$$\therefore \text{K.E. of 1 gm.} \quad \frac{1}{2} C^2 = \frac{3}{2} \frac{RT}{M}$$

$$= \frac{3}{2} \cdot \frac{8.31 \times 10^7 \times 273}{4}$$

$$= 8.5 \times 10^9 \text{ ergs.}$$

7.8. Kinetic Interpretation of Temperature. According to Maxwell's Theorem of Equi-partition of Energy, no matter how many kinds of molecules are mixed together in a gaseous mass, and no matter how widely their weights differ from one another, their repeated collisions with one another must ultimately establish a state of things in which all individual molecules have the same average energy, irrespective of their weights. It does not mean that at any given instant all molecules possess equal energy, but on averaging the energy of all the molecules over a long time (say one second, in which time at least 100 million collisions occur), the average energy of all individual molecules will be found to be the same. The lighter molecules make up for their smaller weights by their higher speeds. This has been confirmed by Graham by measuring the rates at which different molecules stream through an orifice into a vacuum.

It follows from the above that

$$\frac{1}{2} m_1 C_1^2 = \frac{1}{2} m_2 C_2^2 = \frac{1}{2} m_3 C_3^2 = \text{constant,}$$

where m_1, m_2, \dots are the weights of various molecules and C_1, C_2, \dots their velocities.

$$\text{Now } pV = \frac{1}{3} MC^2 = RT \quad (\text{Standard Gas equation})$$

$$\therefore \frac{1}{3} MC^2 = RT.$$

In the case of a single gas if m be the mass of one molecule of the gas, and N the number of molecules in one gram-molecule of it,

$$M = mN.$$

$$\therefore \frac{1}{3} MC^2 = \frac{1}{3} mNC^2 = RT$$

or

$$\frac{1}{2} mC^2 = \frac{3}{2} \frac{R}{N} \cdot T = \frac{3}{2} k.T \quad \dots (i)$$

The only interpretation of this equation is that the absolute temperature T , of a gas is proportional to the mean kinetic energy of translation, $\frac{1}{2} mC^2$, of its molecules. At one fixed temperature, the average kinetic energy of the molecules of a gas will have a fixed value; if by collisions the velocity of some of its molecules is increased that of

others will be correspondingly decreased. The same will be true for a mixture of gases, as explained above.

7.9. Degrees of Freedom. The state of a particle moving in a straight line, say along the x -axis, can be described simply by knowing its displacement along the line. If, however, the particle moves in a plane, we must know its displacement both along the x and the y -axes to describe its motion and for a particle moving in space, we must know the displacements along the x , y and z -axes. This is expressed by saying that the particle has one degree of freedom in the first case, two in the second and three in the third. By the **Degrees of Freedom**¹ of a moving body we mean the number of independent variables that must be known to describe its state of motion completely. It can be shown mathematically that *energy is equally distributed among the various degrees of freedom*.

We have seen (art. 7.8) that the energy associated with a single molecule is $\frac{3}{2} k.T$. Hence the energy associated with each degree of freedom of a molecule is $\frac{1}{2} k.T$.

7.10. Avogadro's hypothesis. If unit volumes of two gases exert, the same pressure then

$$p = \frac{1}{3} m_1 n_1 C_1^2 = \frac{1}{3} m_2 n_2 C_2^2$$

when m_1 and m_2 are the masses and n_1 and n_2 the number of molecules per unit volume.

$$\therefore m_1 n_1 C_1^2 = m_2 n_2 C_2^2 \quad \dots (i)$$

If the gases possess the same temperature, then the average K.E. of their molecules is the same, or

$$\frac{1}{2} m_1 C_1^2 = \frac{1}{2} m_2 C_2^2 \quad \dots \dots (ii)$$

Substituting in (i) we get $n_1 = n_2$

i.e., equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules. This is Avogadro's hypothesis.

7.11. Charles Law from Kinetic Theory. The mean kinetic energy of the molecules of all gases is the same at the same temperature. Hence the rate of change of kinetic energy with temperature will be the same for all gases.

or
$$\frac{d}{dT} (\frac{1}{2} m C^2) = \text{constant} \quad \dots (i)$$

Also from Art. 7.7,

$$pV = \frac{1}{3} M C^2$$

where V is the gram-molecular volume and M is the gram-molecular weight. And $M = m.N$ where m is the mass of one molecule and N the Avogadro number.

$$\begin{aligned} \therefore pV &= \frac{1}{3} N.mC^2 \\ &= \frac{2}{3} \cdot N.(\frac{1}{2} mC^2) \end{aligned}$$

1. Degree of Freedom has a different meaning in Phase Rule,

$$\begin{aligned}\therefore \frac{d}{dT}(pV) &= \frac{d}{dT} \left[\frac{2}{3} N \left(\frac{1}{2} m C^2 \right) \right] \\ &= \frac{2}{3} N \cdot \frac{d}{dT} \left(\frac{1}{2} m C^2 \right)\end{aligned}$$

Substituting from (i)

$$\frac{d}{dT}(pV) = \frac{2}{3} N \times \text{constant}.$$

As N does not change with temperature,

$$\frac{d}{dT}(pV) = \text{constant}$$

or the rate of change of the product of pressure and volume with absolute temperature is constant. If pressure be kept constant, it follows that the rate of change of volume with absolute temperature is constant

$$V \propto T$$

or

This is **Charles Law**.

7.12. Equation $pV = N.k.T$. The kinetic energy of a gas-molecule is proportional to its absolute temperature

$$\text{or} \quad \frac{1}{2} m C^2 = \frac{3}{2} k T$$

also

$$p = \frac{1}{3} m n C^2$$

\therefore

$$p = \frac{1}{3} n \cdot 3 k T$$

$$= n k T \dots \dots \dots (i)$$

where n denotes the number of molecules per unit volume. If there are N molecules in a volume V , (i) becomes

$$pV = N.k.T.$$

This equation embodies the Boyle's, Charles and Avogadro's Laws in one.

7.13. Atomicity of gases. The total translational kinetic energy for a gram molecule of a gas at temperature T is

$$\frac{1}{2} M C^2 = \frac{3}{2} R T$$

and therefore for one gram

$$\frac{1}{2} \cdot 1 \cdot C^2 = \frac{3}{2} r \cdot T, \text{ where } r \text{ is the gas-constant for}$$

one gram of a gas.

The increase in this energy for a rise of temperature of 1°C is $\frac{3}{2}r$. When a gas is heated at constant volume, no heat is used up for doing any external work but the whole of it is used up in raising the temperature of the gas. If r be expressed in heat units, $\frac{3}{2}r$ is the heat required to raise the temperature of one gram of a gas through 1°C or it is the specific heat, C_v , of the gas.

$$\text{Now} \quad Cp - Cv = r$$

$$\text{or} \quad Cp = Cv + r = \frac{3}{2}r + r = \frac{5}{2}r$$

$$\text{and } \gamma = Cp/Cv = \frac{5}{2}r/\frac{3}{2}r = \frac{5}{3} \text{ or } 1.67.$$

This is true for the mon-atomic gases like Helium or Argon.

In the case of gases whose molecules consist of more than one atom (*e.g.*, Oxygen and Hydrogen are di-atomic), the atoms may *spin* in addition to moving bodily *i.e.*, possess both translational and rotational kinetic energy. When such a gas is heated, energy absorbed by it is shared both by the rotation and the translation of its molecules, but it is only the *later* that produces a rise of temperature. Therefore in such cases, an extra amount of energy is always absorbed to augment the energy of rotation of molecules or $C_v > \frac{3}{2}r$ by just this amount.

A di-atomic gas molecule possesses three degrees of translational motion. In addition, the system is also capable of rotating about any of the two axes perpendicular to the line of centres of the two constituent atoms a, a , *i.e.*, about the line PP or about a line perpendicular to both PP , and aa . It has altogether *five* degrees of freedom. The energy associated with one gram of a gas (having N' molecules) is

$$5.N' \cdot \frac{1}{2}kT = \frac{5}{2}r.T$$

$$\therefore C_p = \frac{5}{2}r + r$$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}r + r}{\frac{5}{2}r} = \frac{7}{5} = 1.4$$

Fig. 7.5
Degrees of Freedom of di-atomic molecule and

A triatomic molecule has *three* rotational degrees of freedom or in all six degree of freedom and

$$\gamma = \frac{\frac{6}{2}r + r}{\frac{6}{2}r} = 1.33.$$

QUESTIONS

1. Write a brief note on the kinetic theory of matter. Explain 'the equilibrium in saturated vapours is dynamic'.
2. Deduce an expression for the pressure exerted by an ideal gas in terms of the velocity of its molecules.
3. Prove the Boyle's Law for gases, starting from kinetic considerations and show that temperature of a gas is proportional to (speed)² of its molecules.
4. Calculate the velocity of the molecules of hydrogen gas at 15°C, given that one litre of the gas weighs 0.086 gm. at 15°C, and under normal pressure.
[Hint $\rho = 0.086 \div 1000$]
5. Determine the r.m.s. velocity of oxygen molecules at 15°C., given that the molecular weight of oxygen is 32 gm.
6. Write a note on the kinetic interpretation of temperature.
7. How will you deduce Avogadro's hypothesis from the kinetic theory of gases?
8. Deduce Charles law for gases from kinetic considerations.
9. Write a comprehensive note on the kinetic theory of gases.
10. Discuss the Maxwellian distribution of molecular velocities in gases. How has it been experimentally confirmed by Zartman.
11. Write a note on the liquid and solid states of matter.
What is Brownian Movement and what light does it throw on the molecular movements in liquids.
12. What light does the magnitude of $C_p/C_v = \gamma$ throw on the atomicity of gases.

CHAPTER VIII

CONTINUITY OF STATE

Nature knows nothing of sharp dividing lines ; they are invariably the creation of the human mind.—*Barton.*

8.1. For a long time liquids and gases had been supposed to be two distinct states of matter having nothing in common in their behaviour. The liquids possess the distinctive property of presenting a free surface and are practically incompressible. The cohesive forces between liquid molecules are very strong. That is why a given quantity of a liquid has always the same volume under the same conditions. The gases, on the other hand, have no free surface, are highly compressible and obey the Boyle's law. The cohesive forces between the molecules of a gas (unless the gas be highly compressed) are *practically* non-existent. Careful experiments by Regnault and Amagat showed that gases obey the Boyle's law with a fair accuracy, only at ordinary temperatures and pressures, but that under high pressures and at low temperatures marked deviations from the law are observed. The gases appear to be much more compressible, under these trying conditions. That only means that attractive forces between gaseous molecules are becoming significant and if the molecules were to come very much closer together, the transition from the gas to the liquid might become possible.

At about the same time Faraday succeeded in liquefying chlorine gas into an oily liquid under its own pressure. These two experiments point to an essential similarity between the liquid and gaseous states, but the historic experiment of Cagniard de la Tour focussed the attention of the scientific world on this problem.

8.2. de la Tour's Experiment. A quantity of a liquid was enclosed above the mercury contained in a J-shaped tube, as shown. The space above the liquid contained its saturated vapour only and no air whatsoever was present. The tube was placed in a water-bath and gradually heated. The meniscus of the liquid was observed to get flatter and flatter, indicating that the surface tension of the liquid was diminishing. At a certain temperature the free surface of the liquid disappeared altogether and the whole space presented a homogeneous look. That did not necessarily mean that the whole of the liquid had evaporated. It only meant that *the visible physical distinction between the two states had disappeared*. On cooling, a cloud suddenly appeared in the tube. It then vanished leaving the free surface of the liquid behind.



Fig. 36.
de la
Tour's
Experi-
ment.

Andrews then made a systematic study of the effect of temperature and pressure on the volume of gases, in a series of classical experiments extending over a number of years. He showed that *the liquid and gaseous states are only distant stages of a long series of continuous physical changes.*

8.3. Andrews' Experiments.

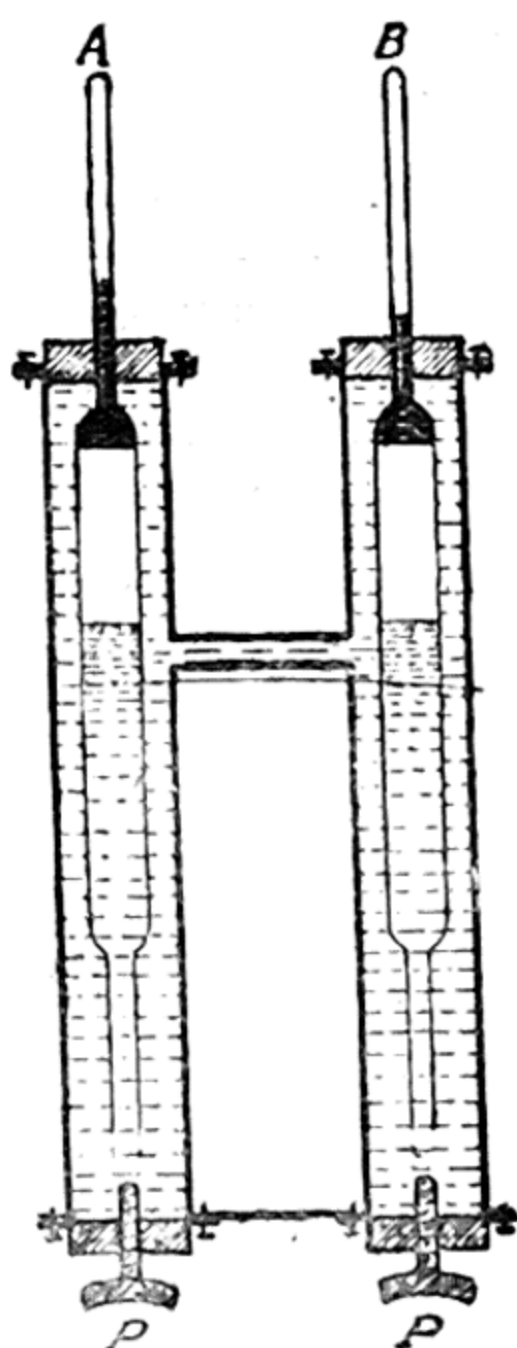


Fig. 8.2
Andrews' experiment

His apparatus consisted of a pipette-shaped strong glass tube *A* whose upper narrow portion was accurately graduated. Pure dry carbon dioxide was passed through it for some hours to remove all traces of air from it and the top was then sealed off. By slightly warming the tube a pallet of mercury was sucked into it which served as a movable stopper.

The tube was then secured in one limb of a strong *H*-shaped steel tube filled with water. A similar tube *B* containing air was secured in the other. *B* was surrounded by a *constant* temperature bath, while the temperature of the bath surrounding *A* could be brought to any desired value. Pressure was gradually applied to the two tubes by means of the screw plungers *PP*, till the mercury was visible just above the steel tubes. The horizontal cross-piece ensured the equality of pressures in the two limbs. The volume of the gas was directly read on *A* while the corresponding pressure was calculated with the help of the air tube *B* which had been calibrated by subjecting it to known pressures (at a constant temperature) in a separate experiment. The pressure on the gas was increased, step by step, by screwing in the plungers and the corresponding volumes were noted. The experiment

was repeated a number of times for various temperatures of the gas. Curves were plotted between corresponding values of pressure and volume for various temperatures. They are called the **isothermals** for carbon dioxide.

3.4. Isothermals for Carbon-Dioxide.

Consider the 13.1° isothermal. The initial volume and pressure of the gas are represented by a point *A*. As the pressure on the gas is gradually increased, at constant temperature, the volume decreases practically in accordance with Boyle's law till the point *B* is reached. If we attempt to compress the gas any further, some of the gas gets liquefied, but *the pressure remains the same*. If this pressure be now maintained constant, more and more of the gas will get liquefied till the point *C* is reached when the liquefaction is complete. After this point, increase of pressure has very little effect on the volume of the liquid and the curve runs practically parallel to the axis of pressure.

The general shape of the 21.5° isothermal is the same but the specific volume (*i.e.*, volume occupied by unit mass) of the vapour

when condensation begins is much smaller, while that of the liquid when the condensation is complete, is larger than the corresponding volume for the previous curve. As the temperature is raised more and more, the specific volume of the vapour goes on diminishing while that of the liquid goes on increasing till at a certain temperature the two volumes become equal. Thus in the 31.1° isothermal, the horizontal part has just disappeared and the specific volumes of the vapour and liquid have become identical. This is called the *critical isothermal* and the corresponding temperature, the *critical temperature*.

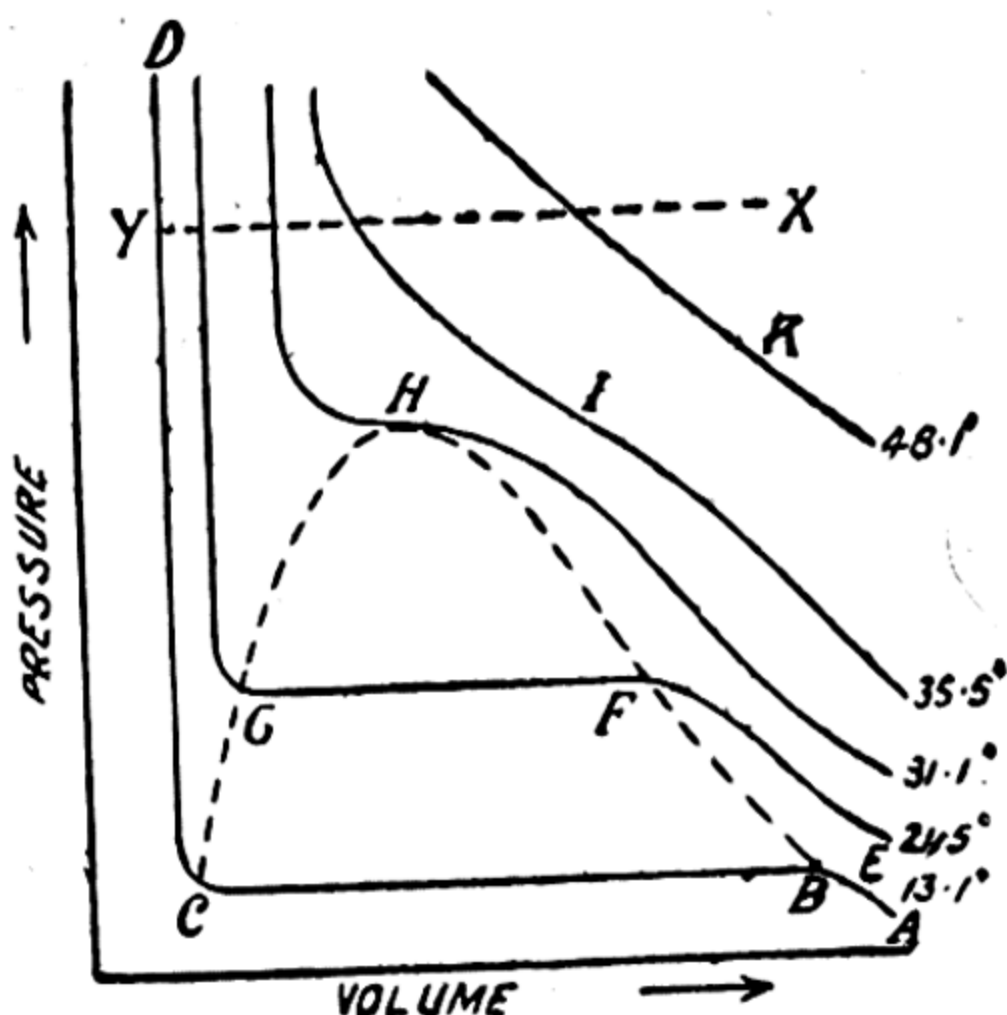


Fig. 8.3
Isotherms for CO_2 .

The horizontal portion is not visible in the 35.5° isothermal and no separation of the liquid occurs. It will, however, be seen that the volume runs down rapidly in the central portion of the isothermal. At still higher temperatures even this peculiarity of the isotherms disappears and they resemble the ordinary isotherms for air.

It is apparent from the above, that the properties of gases and vapours approximate to each other as the temperature is raised from very low initial values and become identical at the critical temperature. It is even possible to pass from the gaseous to the liquid condition without any discontinuity being observed. Thus if a volume X of the gas be cooled steadily at *constant pressure*, the volume will steadily diminish till a point Y , which corresponds to the liquid condition, is reached without a discontinuity occurring anywhere. This establishes the continuity of the liquid and gaseous states.

8.5. Further Considerations. If we plot the values of pv against p at constant temperature for carbon dioxide, it is observed that for temperatures round about its critical temperature, pv first decreases as p increases, reaches a minimum value and then begins to show an increase for larger pressures. This peculiarity becomes less marked at higher temperatures. For temperatures far removed from the critical temperature, the form of the curves is similar to that for the more permanent gases like oxygen and nitrogen.

Careful experiments carried out by Holborn on several gases up to pressures of 1,000 atmospheres and temperatures varying from -180°C to 400°C and similar experiments conducted by K. Onnes at very low temperatures show that no gas obeys the Boyle's law accurately

at all temperatures. The behaviour of all actual gases on compression at constant temperature, can be represented by an equation of the type

$$pv = A + Bp + Cp^2 + Dp^3 + \dots$$

where $A = RT$, and B, C, D are constants for a fixed temperature but decrease rapidly for higher temperatures. They are called *Virial coefficients*. The most important coefficient is B . For all gases B is negative at low temperatures, but gradually increases to zero and becomes positive for higher temperatures. The temperature for which B is zero is called the *Boyle temperature*. At this temperature gases obey Boyle's law over a wide range of pressures. The Boyle temperature for nitrogen is 50°C , for hydrogen it is -164°C and for helium -250°C . Thus

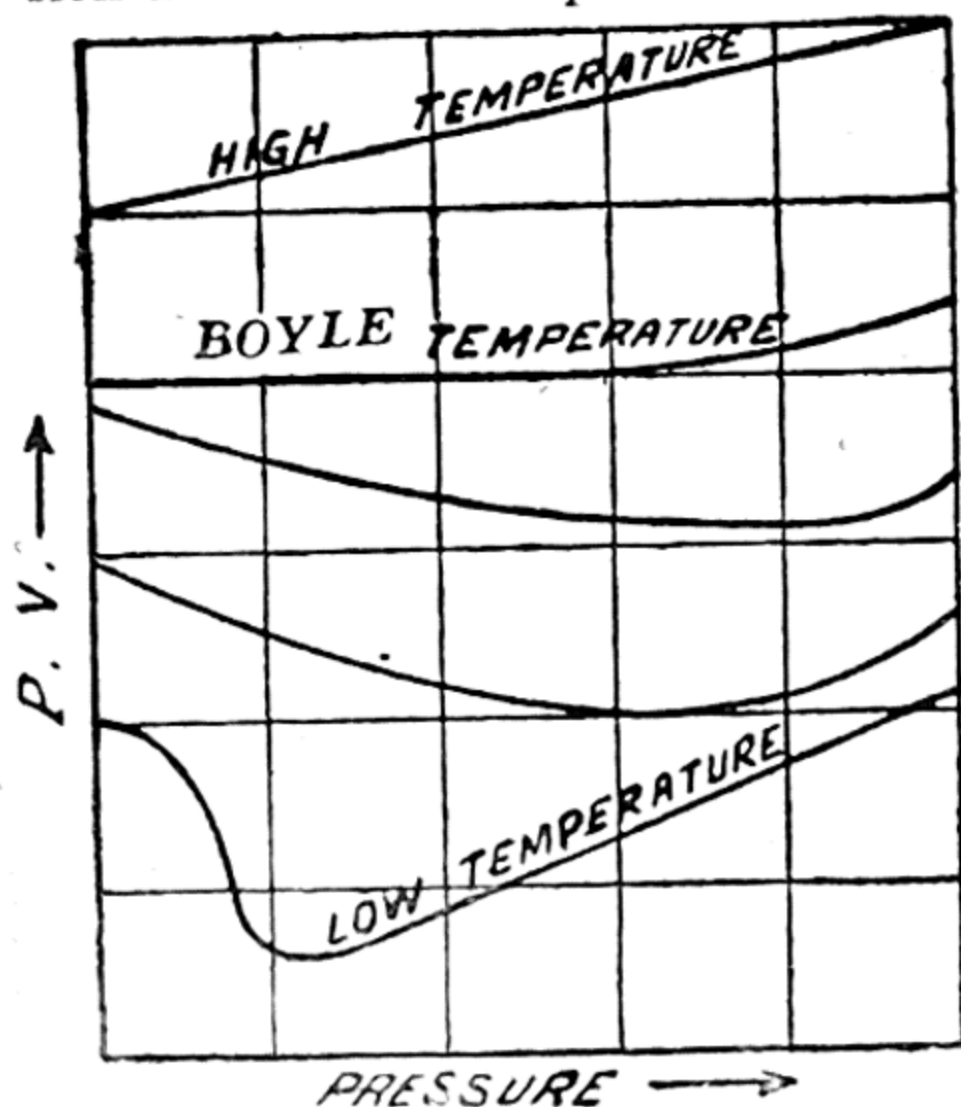


Fig. 8.4
(p - pv curves for gases)

$$\frac{d(pv)}{dp} = 0 + B,$$

neglecting the other terms because their coefficients C, D, \dots are very small, and if $B = 0$, pv must be constant for that temperature, otherwise its differential coefficient with respect to p will not be zero. This fact can be observed in the relevant curve. The fact that actual gases are more compressible than an ideal gas suggests the possibility of the existence of inter-molecular attraction. This attraction becomes apparent only when higher compressions bring the molecules closer together. That inter-molecular attraction actually exists in gases, was confirmed by the Porous-plug Experiment (See Chapter X).

8.6. Van der Waals' Equation (1873). In deriving the ideal gas equation $PV = RT$, we have neither taken into consideration the finite size of the molecules, nor their mutual attractions; we have supposed that *the molecules are material points, which do not interact with one another*. The result is that no actual gas rigorously conforms to the above equation. Van der Waals corrected the above equation by making allowance for both these factors.

(1) **Correction for mutual attraction of molecules.** In the interior of a mass of gas a molecule moves freely. It is pulled equally in all directions by the surrounding molecules. The resultant pull on it is zero because the various forces merely cancel one another. Conditions are, however, different at the confines of the gas. A molecule A , at the boundary, experiences a backward pull from the molecules lying behind it and slows down with the result that it strikes the wall of the containing vessel with a velocity

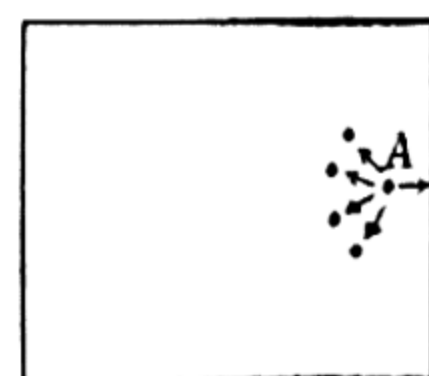
less than that of the molecules in the interior of the gas and therefore produces a lesser pressure. Hence in our equation we must add to the pressure P which is actually exerted by the gas on the walls of the vessel, a term α equal to the decrease of pressure produced by molecular attraction. This α depends on the product of (i) the force exerted on a molecule by those lying behind it and (ii) the number of molecules striking unit area of the wall per second. Each of these factors depends upon the number of molecules in a unit volume of the gas, i.e., on its density D , hence

$$\alpha \propto D^2$$

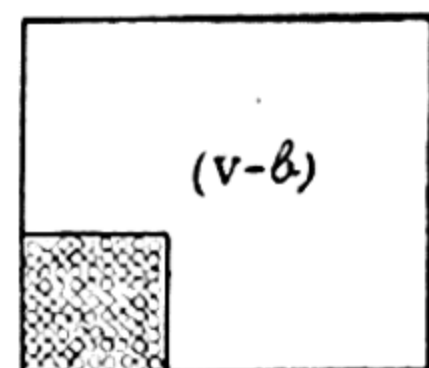
since density is inversely proportional to the volume,

$$\alpha = \frac{a}{V^2} \text{ where } a \text{ is constant}$$

Hence the corrected pressure is $\left(P + \frac{a}{V^2} \right)$



(i)



(ii)

Fig. 8.5. To illustrate Van der Waal's equation

(2) **Correction for finite size of the molecules.** The fact that the molecules have a finite size decreases the space available to them for free movement and since molecules are incompressible, the effect becomes very marked when the gas is highly compressed. What is decreased by an increase of pressure is not the *whole* volume which the gas is occupying, but only that part of it viz. $(V-b)$, which the molecules are *not* occupying. It has been calculated that b is not the

actual volume of the molecules but four times that volume because each molecule is surrounded by a 'sphere of influence' of radius equal to the diameter of the molecule and the centre of any other molecule cannot come within it, because even when two molecules touch each other, their centres, A and B , are apart a distance equal to the sum of their radii. The volume of this sphere $\frac{4}{3}\pi(2r)^3$ is eight times the volume $\frac{4}{3}\pi r^3$ of a single molecule or four times the volume of the pair of molecules involved in the collision. Taking all the molecules in such pairs, it is clear that the forbidden volume is four times the volume of all the molecules. Moreover, the molecules of a gas are in constant motion and the effect of this motion also is to increase the volume correction.

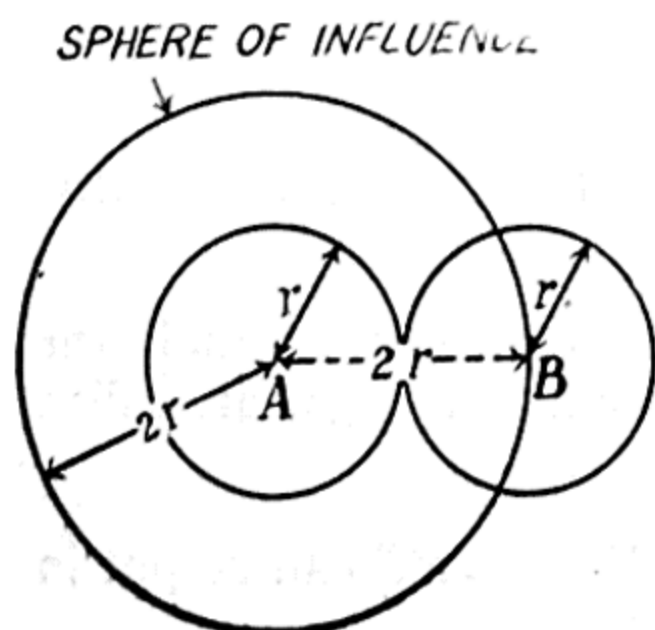


Fig. 8.6

Sphere of Influence

Hence the corrected Gas-Equation is

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT.$$

This is known as the van der Waals' equation. It was a bold and valuable attempt to make the Gas-equation fit the behaviour of actual gases, but in spite of general agreement, deductions from this

equation show great departure from experimental results. In fact, experiment has shown that a and b are not constants. They change with temperature ; especially ' a ' decreases as the temperature rises.

The van der Waals' equation can be represented graphically as shown. These curves differ from the Andrews' curves in giving maxima and minima in place of the horizontal portions of the latter. There is thus a difference between theory and experiment. We can, however give an explanation for this divergence. The portion CD represents the unstable state called supersaturated vapour while the portion AB , the unstable state called super-heated liquid. Both these states (though unstable) can be realized in practice. The portion CB , however, depicts the decrease of volume with decrease of pressure, which can never be realized in practice.

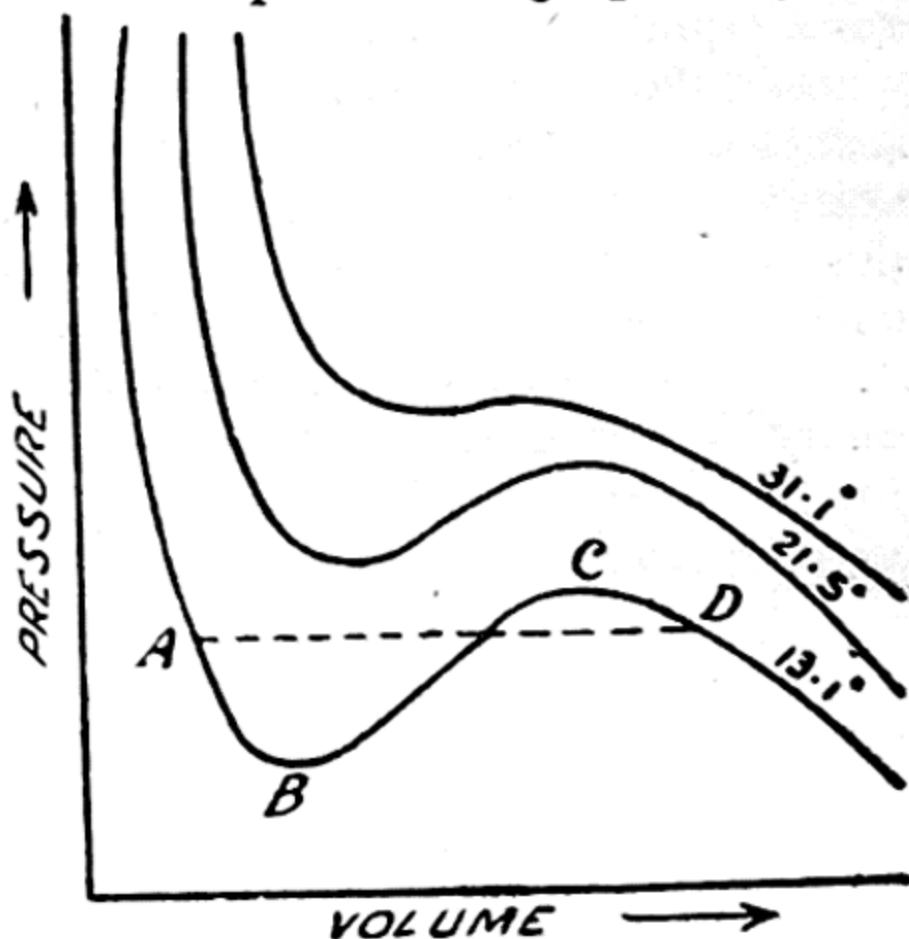


Fig. 8.7
Theoretical curves for CO_2

It will, however, be seen that at higher temperatures the two families of curves tend to be identical.

Dieterici has proposed the equation

$$P(V-b) = RT.e^{-\frac{a}{RTV}}$$

It shows a somewhat better agreement with experimental results, but still the agreement is not complete.

8.7. Critical Constants. The critical temperature and the corresponding values of the pressure and volume of a gas are called **critical constants**.

Van der Waals' equation $\left(P + \frac{a}{V^2}\right)(V-b) = RT$ can be put in the form

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0 \quad \dots \dots (i)$$

This being a cubic equation has three roots which will be coincident at the critical temperature. Let p, v, t , be the critical values of P, V, T . Then for three equal roots

$$(V-v)^3 = 0$$

$$\text{or} \quad V^3 - 3v.V^2 + 3v^2V - v^3 = 0 \quad \dots \dots (ii)$$

Also at the critical temperature (i) becomes

$$V^3 - \left(b + \frac{Rt}{p}\right)V^2 + \frac{a}{p}V - \frac{ab}{p} = 0 \quad \dots \dots (iii)$$

Equating the coefficients of like terms in (ii) and (iii)

$$3v = b + \frac{Rt}{p} \quad \dots \quad \dots \quad \dots \quad \dots \quad (iv)$$

$$3v^2 = \frac{a}{p} \quad \dots \quad \dots \quad \dots \quad \dots \quad (v)$$

$$v^3 = \frac{ab}{p} \quad \dots \quad \dots \quad \dots \quad \dots \quad (vi)$$

dividing (vi) by (v) $\frac{v}{3} = b$ or $v = 3b$ $\dots \dots \dots$ (I)

From (v) $p = \frac{a}{3v^2} = \frac{a}{3(3b)^2} = \frac{a}{27b^2} \dots \dots \dots$ (II)

From (iv) $\frac{Rt}{p} = 3v - b = 3.3b - b = 8b.$

$$\therefore t = p \cdot \frac{8b}{R} = \frac{a}{27b^2} \cdot \frac{8b}{R} = \frac{8a}{27Rb} \dots \dots \dots (III)$$

Two different substances are said to be in **corresponding state** when the ratios between their actual pressure, volume and temperature (P, V, T) and their critical pressure, volume and temperature (p, v, t) are the same for both substances.

i.e., $\frac{P}{p} = \frac{T}{t} = \frac{V}{v} = K.$

8.8. Reduced Equation of State. Expressing pressure, volume and temperature of a gas as fractions of their critical values.

$$P = \lambda p \quad V = \mu v \quad T = \nu t$$

and substituting these values in the van der Waals' equation

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT$$

we get

$$\left(\lambda p + \frac{a}{\mu^2 v^2} \right) (\mu v - b) = R \cdot \nu \cdot t$$

Substituting the values of p, v, t , in the above relation, we get

$$\left(\lambda \cdot \frac{a}{27b^2} + \frac{a}{9\mu^2 b^2} \right) (3\mu b - b) = \nu \cdot R \cdot \frac{8a}{27Rb}$$

Dividing throughout by $\frac{a}{27b}$, we have

$$\left(\lambda + \frac{3}{\mu^2} \right) (3\mu - 1) = 8\nu \quad \dots \quad \dots \quad \dots \quad (i)$$

This is the *reduced equation of a gas*. In this equation all the constants— a, b, R —characteristic of any particular substance have disappeared. Hence this equation represents the behaviour of all gases. If we plot on a curve the values of λ and μ for definite values of T , isothermal lines so obtained are common to all substances and are called *Reduced Isothermals* and when λ, μ and ν are each unity, the isothermal so obtained passes through the critical point.

It is clear from equation (i) that if two gases have the same values for any *two* of the quantities λ , μ , ν , they will have the same value for the third also. Thus if two gases have the same reduced pressure and volume, they will also have the same reduced temperature.

QUESTIONS.

1. What is continuity of state? How was it established by Andrews?

2. Give the details of Andrews' experiments on carbon dioxide and explain with a sketch the general form of the isothermals. What is critical temperature.

3. Account for the failure of Boyle's law to fit the behaviour of actual gases.

Deduce the van der Waals' equation and explain the significance of the correction terms.

4. Derive the reduced equation of a gas from the van der Waals' equation and show that if two gases have the same reduced pressure and volume, they will also have the same reduced temperature.

5. Calculate the critical temperature of carbon dioxide given that $a = \cdot 00717$, $b = \cdot 00191$, the unit of pressure being the atmosphere and the unit of volume being the volume of 1 gm. of the gas at N. T. P.

[Using van der Waals equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$\left(1 + \frac{\cdot 00717}{V^2}\right)(1 - \cdot 00191) = R \times 273$$

$$\text{or } R = \frac{1 \cdot 005}{273}$$

The critical temperature

$$t = \frac{8a}{27Rb}$$

$$= \frac{8 \times \cdot 00717 \times 273}{27 \times 1 \cdot 005 \times \cdot 00191}$$

$$= 302 \cdot 1^\circ A$$

$$= 29 \cdot 1^\circ C]$$

CHAPTER IX

ISOTHERMAL AND ADIABATIC OPERATIONS

It is the great beauty of our science that advancement in it whether in a degree great and small, instead of exhausting the subject of research, opens the doors to further and more abundant knowledge, over-flowing with beauty and utility.—*Michael Faraday*.

9.1. Equation of State. A simple system like a gas or a liquid in static condition, is one which can be completely defined by its pressure, volume and temperature (called the *three Parameters*). In other words, for every simple system there always exists a functional relationship between its temperature, pressure and volume which is called the **Equation of State** of the system or $P=f(V,T)$. Each of the three variables can be regarded as a function of the other two and each such functional relationship will be an equation of state of the system.

9.2. Isothermal Operations. Those physical changes which take place in such a manner that the temperature of the substance undergoing the change remains constant throughout the operations, are called *isothermal operations*. The substance remains throughout in good thermal contact with its surroundings. While undergoing such a change, the substance absorbs the equivalent amount of heat from its surroundings when doing external work, but rejects it to them when work is done on it. The Boyle's law is an example of such a change.

The curves depicting the variation in the volume of a substance when the pressure acting on it changes, but its temperature remains constant, are called *Isothermals*.

9.3. Adiabatic Operations. Those physical changes which take place in such a manner that the substance undergoing the change neither absorbs heat from its surroundings nor rejects it to them are called *Adiabatic operations*. The body remains thermally insulated from its surroundings and cannot gain or lose heat *as such* by conduction or radiation or by any other, process. When doing external work, the substance has to draw on its own store of energy and its temperature consequently falls, but when work is done on it, its store of energy increases and its temperature rises. Thus we find that *during such operations the heat content of a body does change*, the only limitation being that no direct exchange of heat can take place between the body and its surroundings. Propagation of sound waves through air is adiabatic. The expansion of the enclosed air when a motor tyre bursts is approximately adiabatic.

The curves depicting the variation in the volume of a substance while the pressure acting on it changes under adiabatic conditions, are called *Adiabatics*.

9.4. Equation to Isothermal for an Ideal Gas. The changes in the volume of an ideal gas when subjected to a varying pressure at *constant temperature* are represented, as already shown, by the equation

$$PV = RT \quad \dots (i)$$

Now R is a constant, and since T is now also a constant, the equation (i) become

$$PV = \text{constant.}$$

i.e., the product of pressure and volume of a definite mass of a gas remains constant under isothermal conditions.

9.5. Equation to Adiabatic for an Ideal Gas. Since in the case under consideration the gas is thermally insulated from its surroundings the *decrease* in its internal energy, dU , will be equivalent to the external work done by it. If the volume of the gas increases by dv against an external pressure p , the work done by it, is $p.dv$, hence

$$-dU = p.dv. \quad \dots \dots \dots (i)$$

Since the internal energy of a perfect gas depends only on its temperature (inter-molecular attraction being absent), the decrease of internal energy per unit mass of the gas will be equal to the product of its specific heat at constant volume and the fall dT in its temperature. Therefore

$$dU = 1.C_v.dT$$

Hence from (i) $C_v.dT + p.dv = 0. \quad \dots \dots \dots (ii)$
which is the equation to the required adiabatic.

Since an ideal gas also satisfies the relation

$$pv = rT$$

we have by differentiation

$$p.dv + v.dp = r.dT.$$

or $dT = \frac{p.dv + v.dp}{r} \quad \dots \dots \dots (ii)$

Putting this value in (ii),

$$C_v. \frac{p.dv + v.dp}{r} + p.dv = 0.$$

or $C_v.p.dv + C_v.v.dp + r.p.dv = 0.$

But $C_p - C_v = r$

Hence $C_v.p.dv + C_v.v.dp + (C_p - C_v)p.dv = 0$

i.e., $C_v.v.dp + C_p.p.dv = 0$

or $\frac{dp}{p} + \frac{C_p}{C_v} \cdot \frac{dv}{v} = 0.$

or $\frac{dp}{p} + \gamma \frac{dv}{v} = 0$, where $\gamma = C_p/C_v.$

Integrating we have

$$\log p + \gamma \log v = \text{constant.}$$

or $\log p \cdot v^\gamma = \text{constant}$

i.e. $p v^\gamma = \text{constant.} \quad \checkmark \quad \dots \quad \dots \quad \text{(I)}$

which is a more convenient and the usual form.

There are two other forms of the above relation. Thus from $p v = r T$, we have

$$p = \frac{r T}{v}$$

Hence from (I) $\frac{r T}{v} \cdot v^\gamma = \text{constant.}$

or $T v^{\gamma-1} = \text{constant.} \quad \dots \quad \dots \quad \text{(II)}$

Similarly $v = \frac{r \cdot T}{p}$

and $p \cdot \left(\frac{r \cdot T}{p} \right)^\gamma = \text{constant}$

$\therefore \frac{p^{\gamma-1}}{T^\gamma} = \frac{r^\gamma}{\text{constant}} = \text{constant} \quad \dots \quad \dots \quad \text{(III)}$

The above three relations which are *strictly* true for an ideal gas only, can also be used for all actual gases at ordinary temperatures and pressures.

9.6. Example 1. Dry air enclosed at 0°C and atmospheric pressure is suddenly compressed to half its volume. Determine the resulting temperature ($\gamma = 1.4$).

Use the relation connecting T and v under adiabatic conditions i.e.,

$$T_1 v_1^{\gamma-1} = T_2 v_2^{\gamma-1}$$

or $T_2 = T_1 \left(\frac{v_1}{v_2} \right)^{\gamma-1} = 273(2)^{1.4-1}$

$\therefore \log T_2 = \log 273 - .4 \log 2 = 2.4362 + .4 \times .3010 = 2.5566$

$\therefore T_2 = 360.2^\circ\text{A or } 87.2^\circ\text{C.}$

Example 2. Dry air enclosed at 25°C and atmospheric pressure is suddenly compressed to half its volume. Determine the resulting pressure, ($\gamma = 1.4$).

Use the relation connecting p and v under adiabatic conditions i.e.,

$$p_1 v_1^\gamma = p_2 v_2^\gamma$$

or $p_2 = p_1 \left(\frac{v_1}{v_2} \right)^\gamma = 1 \times 2^{1.4}$

$$\therefore \log p_2 = \log 1 + 1.4 \log 2 = 0 + 1.4 \times .3010 = .42140$$

$$\therefore p_2 = 2.636 \text{ atmospheres.}$$

Example 3. Calculate the rise in temperature when a gas ($\gamma = 1.5$) is compressed to eight times its original pressure, assuming the initial temperature to be 27°C .

Use the relation connecting T and p under adiabatic conditions i.e.,

$$\frac{p_1^{\gamma-1}}{T_1^{\gamma}} = \frac{p_2^{\gamma-1}}{T_2^{\gamma}}$$

or

$$\left(\frac{p_2}{p_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^{\gamma}$$

$$(8)^{.5} = \frac{T_2^{1.5}}{(300)^{1.5}} \quad (\because 273 + 27 = 300)$$

$$\therefore 1.5 \log T_2 = .5 \log 8 + 1.5 \log 300$$

$$= .5 \times .9031 + 1.5 \times 2.4771$$

or

$$T_2 = 599.8^\circ\text{A}$$

$$= 326.8^\circ\text{C.}$$

9.7. Work done by a Gas in Expansion. Let S and S' represent the surface of a volume of gas before and after a small expansion against an external pressure \bar{p} , the pressure being constant over the surface. Suppose the pressure of the gas is only slightly greater than the external pressure. This will ensure that the expansion of the gas will be very slow and no energy of motion will be developed.

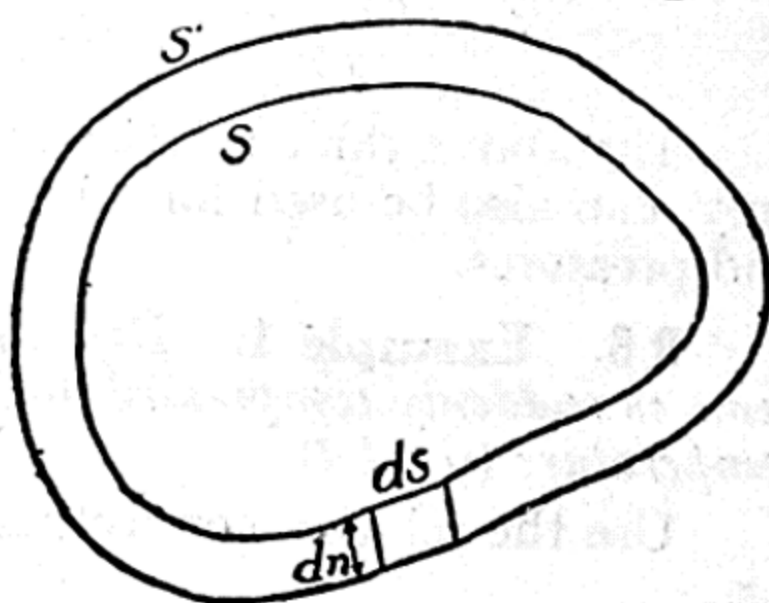


Fig. 9.1

Consider an element ds of surface and let its displacement along the normal be dn . The work done by the gas is then $\Sigma (p ds) dn$

$$= p \Sigma ds \cdot dn$$

$$= p \times (\text{increase of volume})$$

$$= p \cdot dv.$$

(1) If the gas expands *isothermally* from a volume v_a to a volume

v_b , the work done is $\int_{v_a}^{v_b} p dv$

But $p v = R T = K$, a constant, since T is constant

hence $p = \frac{K}{v}$

$$\therefore \text{Work done} = \int_{v_a}^{v_b} \frac{K}{v} \cdot dv$$

$$= K \log_e \frac{v_b}{v_a}$$

$$= RT \log_e \frac{v_b}{v_a} = p_a \cdot v_a \log_e \frac{v_b}{v_a} \text{ ergs.}$$

(2) If the gas expands *adiabatically*, work done is

$$\int_{v_a}^{v_b} p dv$$

Since $pv^\gamma = K$, $p = \frac{K}{v^\gamma}$

$$\therefore \text{Work done} = K \int_{v_a}^{v_b} \frac{dv}{v^\gamma}$$

$$= \frac{K}{1-\gamma} \left[\frac{1}{\gamma-1} \frac{1}{v_b} - \frac{1}{\gamma-1} \frac{1}{v_a} \right]$$

Putting $K = pv^\gamma$, work done = $\frac{1}{\gamma-1} [p_b \cdot v_b - p_a \cdot v_a]$

$$= \frac{R(T' - T)}{\gamma - 1} \text{ ergs, where } T \text{ and } T' \text{ are the initial and final temperatures of the gas respectively.}$$

9.8. Slope of the Adiabatic for an Ideal Gas. Differentiating $pv^\gamma = \text{constant}$, we have

$$p \cdot \gamma \cdot v^{\gamma-1} dv + v^\gamma dp = 0$$

$$\text{or the slope } \frac{dp}{dv} = -\gamma \frac{p}{v} \quad \dots \quad (i)$$

Similarly, differentiating the isothermal relation $pv = \text{constant}$, we have

$$p dv + v dp = 0$$

and the slope $\frac{dp}{dv} = -\frac{p}{v} \quad \dots \quad (ii)$

Comparing (i) and (ii) we find that the slope of an adiabatic is γ times the slope of the corresponding isothermal and since $\gamma (=C_p/C_v)$ is always greater than unity, the adiabatic is always steeper than the isothermal at the point where the two curves intersect each other.

9.9. Isothermal and adiabatic elasticity of a gas. The elasticity of a gas is given by ratio of the change in its pressure to the fractional change in its volume. Thus if on increasing the pressure

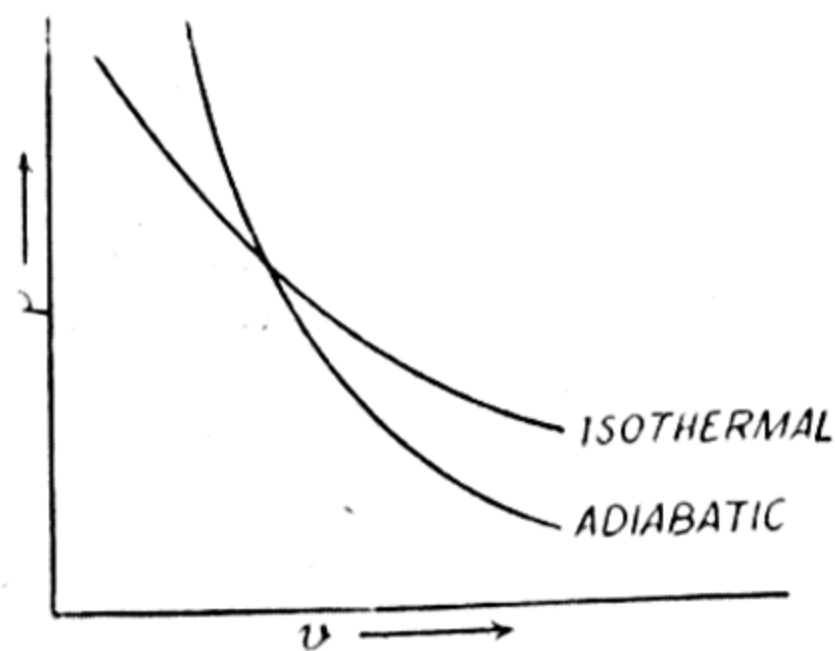


Fig. 9.2

Adiabatic steeper than isotherm

on a gas from p to $p+dp$ the volume changes from v to $v-dv$,

$$\text{Elasticity} = dp / \left(\frac{-dv}{v} \right).$$

(i) *Isothermal elasticity.* The equation to the isothermal for a gas is

$$pv = \text{constant}$$

Differentiating, $p dv + v dp = 0$

and $dp / \left(\frac{-dv}{v} \right) = p$

or the isothermal elasticity of a gas equals its pressure.

(ii) *Adiabatic elasticity.* The equation to the adiabatic for a gas is

$$pv^\gamma = \text{constant}.$$

Differentiating,

$$p \cdot \gamma v^{\gamma-1} dv + v^\gamma \cdot dp = 0$$

and

$$dp / \left(\frac{-dv}{v} \right) = \gamma \cdot p$$

or the adiabatic elasticity of a gas equals γ times the pressure, where $\gamma = C_p/C_v$, is the ratio between the two principal specific heats of a gas.

9.10. Clement and Desormes' Method for γ . The ratio between the two specific heats of a gas i.e., $\gamma = C_p/C_v$ was first directly determined by Clement and Desormes.

The gas is contained in a large vessel of over 20 litres capacity at a pressure a little above the atmospheric. The vessel is provided with a stop-cock of wide bore and is connected to a sulphuric acid gauge by means of a side-tube. To reduce the loss of heat from its surface, the vessel is plugged with cotton-wool. Air is pumped into the vessel with a foot-bellows so as to produce a pressure-difference of about 10 cm. in the gauge. This pressure is measured a few minutes later so that the air inside may cool down to the atmospheric temperature. The stop-cock is then opened and quickly closed again. The gas expands adiabatically to the atmospheric pressure and suffers a fall in temperature. This lowering of temperature is difficult to measure with exactness because almost at once the gas begins to gain heat from the outside by conduction. Clement and Desormes avoided this temperature-measurement by allowing the gas to warm up, at constant volume, to the room temperature again. In doing so, the pressure of the gas rose and the maximum pressure, p_2 , reached was noted.

Let p_1 be the initial pressure of the gas and T_1 the initial (room) temperature and let p_0 be the atmospheric pressure and T_0 the temperature reached after the adiabatic expansion, then

$$\frac{p_1^{\gamma-1}}{T_1^\gamma} = \frac{p_0^{\gamma-1}}{T_0^\gamma} \text{ or } \left(\frac{p_1}{p_0}\right)^{\gamma-1} = \left(\frac{T_1}{T_0}\right)^\gamma \quad \dots(i)$$

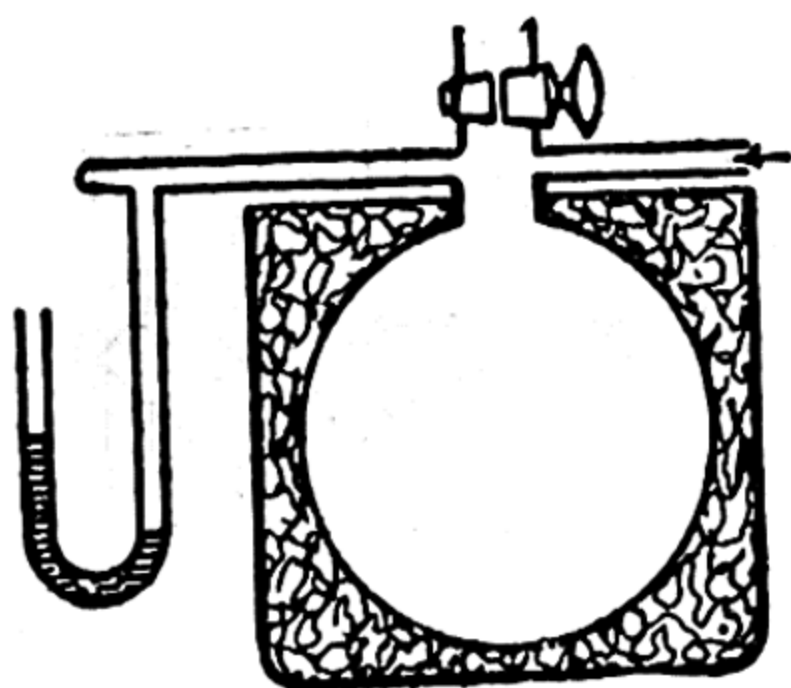


Fig. 9.3
Clement and Desorme's
Apparatus.

Again, since the gas warms up at constant volume to the temperature T_1 and pressure p_2

$$\frac{p_2}{p_0} = \frac{T_1}{T_0}$$

Substituting in (i) we have

$$\left(\frac{p_1}{p_0}\right)^{\gamma-1} = \left(\frac{p_2}{p_0}\right)^\gamma$$

$$\therefore (\gamma-1)(\log p_1 - \log p_0) = \gamma(\log p_2 - \log p_0)$$

$$\gamma = \frac{\log p_1 - \log p_0}{\log p_1 - \log p_2} \quad (ii)$$

or

Since the pressure-differences indicated by the gauge are very small as compared with the atmospheric pressure p_0 , we can make an approximation. Let $p_1 = p_0 + H$ and $p_2 = p_0 + h$, Substituting in (ii), we have

$$\gamma = \log_e \frac{p_0 + H}{p_0} / \log_e \frac{p_0 + H}{p_0 + h}$$

$$= \log_e \left(1 + \frac{H}{p_0}\right) / \log_e \left(1 + \frac{H-h}{p_0 + h}\right)$$

$$= \left(\frac{H}{p_0} - \frac{H^2}{2p_0^2} + \dots\right) / \left(\frac{H-h}{p_0 + h} - \frac{(H-h)^2}{2(p_0 + h)^2} + \dots\right)$$

since $\frac{H}{p_0}$ and $\frac{H-h}{p_0 + h}$ are < 1 .

hence neglecting terms of the second and higher degrees, we get

$$\gamma = \frac{H}{p_0} / \frac{H-h}{p_0 + h}$$

Again neglecting h , in the term $(p_0 + h)$, because it is very small as compared with p_0 , we have.

$$\gamma = \frac{H}{H-h}$$

The above relationship is fairly accurate and convenient to use for the laboratory determination of γ .

The above experiment is open to one serious objection. When the stop-cock is opened, a series of oscillations are set up in the air in the neck. When an oscillation moves outwards, the pressure inside falls below atmospheric and when the oscillation moves inwards, the inside pressure exceeds the atmospheric. It is difficult to judge the *exact* instant at which the stop-cock should be closed and therefore the pres-

sure inside may not be atmospheric when the stop-cock is closed. To meet this objection the experiment was modified by Partington.

9.11. Partington's Determination of γ .

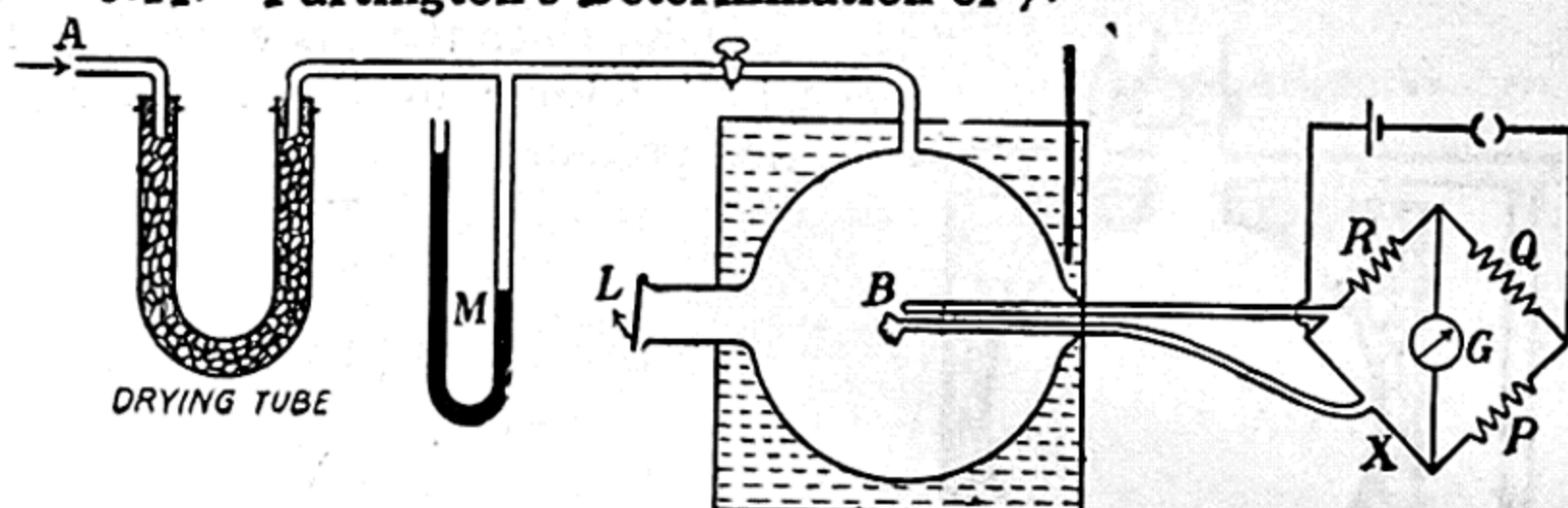


Fig. 9.4.

Partington's Arrangement for γ .

He used a spherical flask of about 130 litres capacity having a mouth of such a size that no oscillations were set up in the contained gas when it was allowed to expand adiabatically on suddenly opening the lid L . The proper size of the opening was determined by trial. A flask of such giant dimensions was used in order to cut down radiation losses from its surface, because while its volume depends on the cube of the radius (volume = $\frac{4}{3}\pi r^3$) the surface-area depends on the square of the radius (surface area = $4\pi r^2$). Thus on trebling the radius, the volume increases 3^3 or 27-fold while the surface area increases 3^2 or 9-fold only. A sensitive bolometer B was placed at the centre of the flask and was joined in the X-arm while the compensating leads were in the R-arm of the wheatstone's bridge arrangement. A string galvanometer was used to indicate the balance because its response is very *quick*. Initially, the bridge was kept *slightly* unbalanced and it was so arranged (by trial) that when the resistance of B diminished due to the adiabatic expansion of the gas in the flask, the bridge should *just* get balanced.

The flask was kept in a constant-temperature water-bath which was well-stirred and whose temperature, T_1 , was recorded by a sensitive thermometer. Pure gas was forced through drying tubes into the flask through A , the pressure difference was read in the manometer and the initial pressure p_1 was determined by adding this difference to the barometric pressure p_0 . The lid L was then opened for a second and closed again. The gas expanded *adiabatically* to the atmospheric pressure p_0 and its temperature fell to T_0 and the bridge was just balanced. Ice was then added to the water-bath in such amounts that its temperature remained constant at T_0 . This was indicated by the bridge remaining balanced. The temperature, T_0 , of the bath was then read by the thermometer placed in the bath. Since the expansion is adiabatic

$$\frac{p_1^{\gamma-1}}{T_1^{\gamma}} = \frac{p_0^{\gamma-1}}{T_0^{\gamma}}$$

$$\left(\frac{p_1}{p_0}\right)^{\gamma-1} = \left(\frac{T_1}{T_0}\right)^{\gamma}$$

or

$$\begin{aligned} \text{or} \quad & (\gamma - 1) [\log p_1 - \log p_0] = \gamma [\log T_1 - \log T_0] \\ \text{or} \quad & \gamma [(\log p_1 - \log p_0) - (\log T_1 - \log T_0)] = [\log p_1 - \log p_0] \\ \text{and} \quad & \gamma = \frac{\log p_1 - \log p_0}{(\log p_1 - \log p_0) - (\log T_1 - \log T_0)} \end{aligned}$$

γ was found to be 1.403 for dry air at 17°C. Due to the uncertainty of the cooling correction, the method cannot be used at high temperatures.

QUESTIONS

1. Distinguish between isothermal and adiabatic processes. Show that the adiabatic is steeper than the isothermal at the point where they cross.

2. Derive an equation for the adiabatic to a perfect gas.

A gas is suddenly compressed to one-fourth of its original volume. Calculate the rise in temperature, the original temperature being 27°C and $\gamma = 1.5$. [300°C.]

3. Explain the Clement and Desormes' method of determining the ratio between the two specific heats of a gas. What are the sources of error in this arrangement and how have they been removed by Partington?

4. Obtain an expression for the work due by a gas when it expands (i) isothermally, (ii) adiabatically.

5. Show that the adiabatic elasticity of a gas is γ times the isothermal elasticity.

6. Carefully describe the Partington' method for determining the value of γ . Can the method be used at high temperatures?

CHAPTER X

POROUS-PLUG EXPERIMENT

The secret of those who make discoveries is to look upon nothing as impossible.—*Humboldt*.

The man who cannot wonder is but a pair of spectacles behind which there is no eye.—*Carlyle*.

10.1. Search for Inter-molecular Attraction (Joule). The fact that under high pressures gases show a greater compression than is demanded by Boyle's law, leads us to suspect the existence of inter-molecular attractions in them. Possibly, the attraction is not very marked under ordinary pressures, but becomes appreciable when higher pressures force the molecules closer together. If so, a cooling will be expected on making a gas expand (say, into a vacuum) without doing any external work. In this case, the gas will use a part of its own energy in separating its molecules against their mutual attractions and will therefore cool down.

To test this point, Joule took two copper cylinders *A* and *B*. Gas was compressed into *A* while *B* was exhausted. The two were joined with a tube having a stop-cock and were dipped in a vessel of water whose temperature was recorded by a very sensitive mercury thermometer. The vessel was *just* big enough to hold the two cylinders, so that the minimum amount of water would be needed to completely submerge the two cylinders. This precaution was taken to ensure the measurement of any temperature change, even if small. As water possesses a large specific heat, any small change in the heat content of the system *AB*, will not produce an appreciable temperature change, if a large quantity of water were used. The stop-cock was opened, the gas from *A* expanded into *B*, but no change in the temperature of water was observed. Joule varied his experiment by immersing *A* and *B* in separate baths, still no trace of inter-molecular attraction was observed. Hence Joule concluded that his measurements *were not sensitive enough to detect* the small changes in temperature that might perhaps occur during such experiments and therefore he could not express any definite opinion about the existence or otherwise of inter-molecular attraction.

In collaboration with Lord Kelvin, he designed an apparatus in which the temperature of the gas itself was directly measured by a delicate platinum resistance thermometer and the use of water as a calorimetric substance was dispensed with. This is the classical *Porous-Plug experiment*.

10.2. Porous-Plug Experiment. It is a delicate piece of apparatus due to Joule and Kelvin for detecting inter-molecular attraction

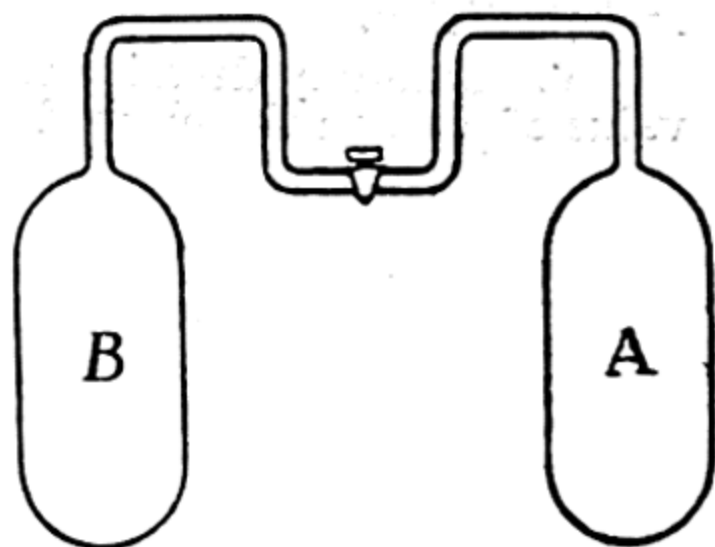


Fig. 10.1.
Joule's Experiment.

in gases. The gas under test is compressed by a pump P into a spiral tube S immersed in a bath of cold water whose temperature is maintained constant. The gas which is heated up by the compression, cools down to the temperature of water as it *slowly* pushes its way through the spiral. It then passes up the wide tube AB across a plug of cotton-wool G which is held in position by two perforated metal discs DD . To prevent the conduction of heat into the plug, this portion of the tube is made of box-wood which is surrounded by a layer of cotton wool WW which is itself surrounded by water. The gas suffers a large drop in pressure in passing through the plug. The plug serves to keep down the velocity of flow of the gas on emergence and also prevents the formation of eddy currents, both of which would entail a loss of energy and produce a cooling of the gas. Care must be taken that no sound is produced when the gas escapes through the plug, because this would also produce a cooling. The flow of the gas is maintained for about an hour in order that temperatures at various points in AB may become constant. The temperature of the gas just before entrance is now recorded by the platinum resistance thermome-

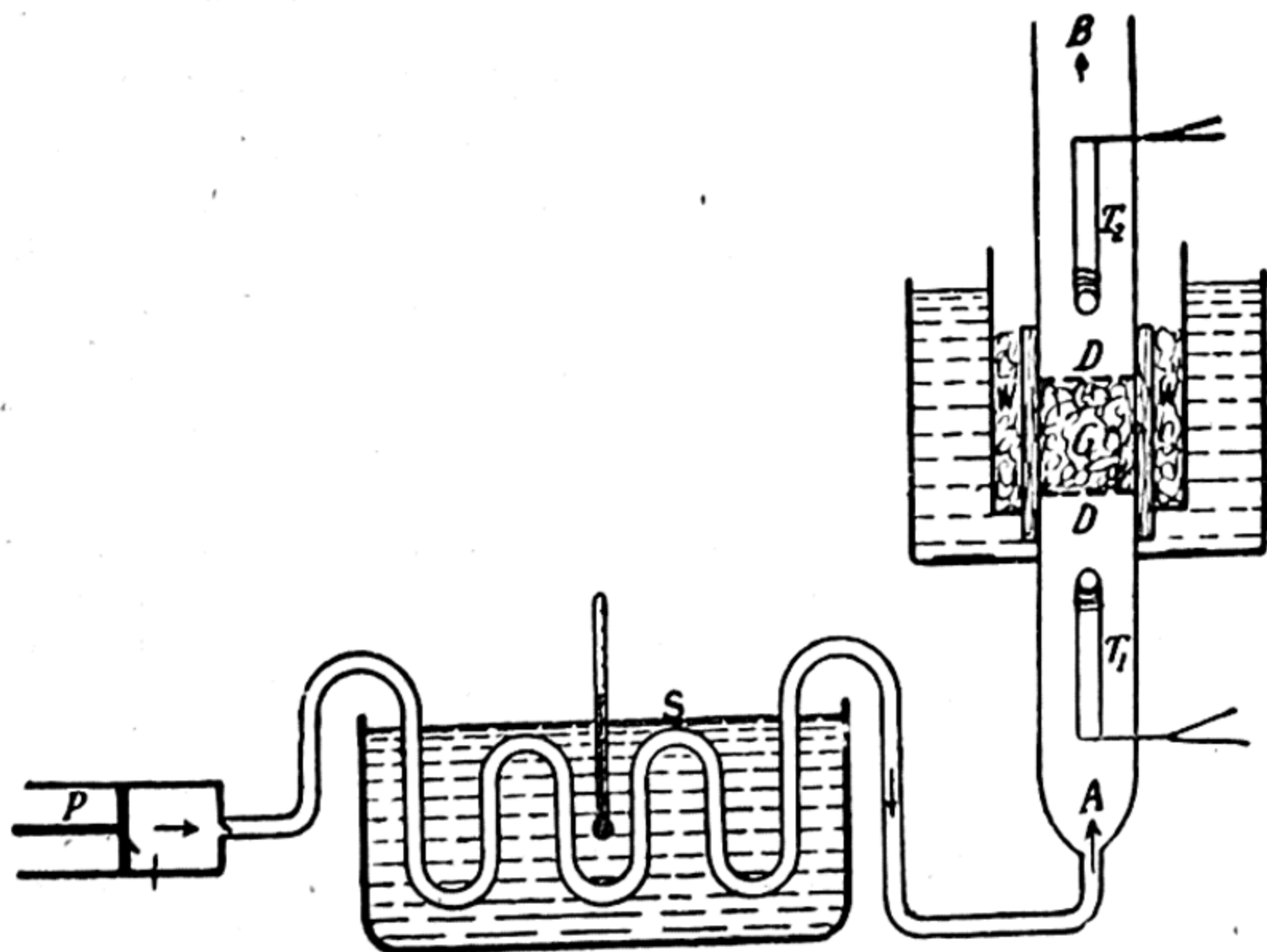


Fig. 10.2. Porous-Plug Experiment.

ter T_1 and on emergence from the plug by the thermometer T_2 , which should be placed a little further away from the plug so that the temperature is measured at a point where the eddies have ceased to exist and gas has been brought to rest by internal friction.

The pressure on the side B being lower than that on the side A the gas expands, but the expansion here is of a type different from that in the Joule's experiment. In the later case the gas expanded into a vacuum without doing any external work while here it expands against a steady external pressure (*e. g.*, that of the atmosphere) and therefore has to do external work. Some extra work *may* have to be

done by the gas in pulling its molecules apart against their mutual attractions, *if such attractions exist*.

In the simple arrangement sketched alongside, P is the porous plug, A is the high pressure side and B the low-pressure side. Let p_1 , v_1 , A_1 be the pressure, volume of a unit mass of gas and area of the piston on the side A , and p_2 , v_2 , A_2 the corresponding quantities on the side B . Suppose a unit mass of the gas is forced through the plug when the piston A moves a distance d to the right. The cross-section of tube B is so

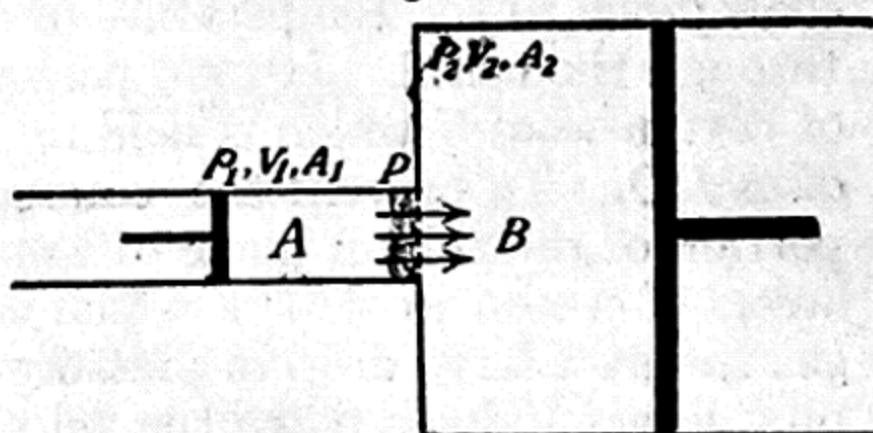


Fig. 10.3.
To illustrate porous plug experiment.

arranged that the piston B also moves a distance d to the right in the meantime. This will ensure that the velocity of the gas remains the same on either side of P and hence also the kinetic energy of its molecules, and no part of the work done by the piston A is used up in producing any such change.

Work done *on the gas* by the piston $A = (p_1 \times A_1)d = p_1(A_1d) = p_1v_1$

Work done *by the gas* on the piston $B = (p_2 \times A_2)d = p_2(A_2d) = p_2v_2$

If it be an ideal gas, p_1v_1 would always be equal to p_2v_2 . Hence work done on the gas would *exactly* cancel that done by the gas itself and no heating or cooling would be expected on that account. A cooling would be expected if the gas had to overcome inter-molecular attractions while expanding; no cooling would be expected if inter-molecular attractions did not exist while a heating would result if the molecules repelled each other.

The problem, however, is not so simple. Actual gases show deviations from Boyle's law and p_v varies with pressure at constant temperature. If $p_2v_2 > p_1v_1$, more work is done by the gas than is done on it. The gas will draw to some extent on its own heat supply and suffer a slight cooling thereby. If $p_2v_2 < p_1v_1$, less work is done by the gas and more work is done on it and there will be a slight heating effect due to this. This heating effect may *just* cancel any cooling due to inter-molecular attractions and no fall of temperature, whatsoever, may be observed. The heating may even more than compensate for the cooling and a slight heating of the gas may actually be observed.

It is thus clear that any change of temperature, due merely to inter-molecular forces, is complicated by the fact that the gas either does a small amount of work while expanding or some work is done on it. Fortunately, it is possible to calculate the later effect from the data made available by Holborn and Onnes. Therefore the *true* Joule-Kelvin effect can be measured.

Joule and Kelvin have found that

(1) A cooling is produced in all gases except in hydrogen which shows a slight rise of temperature. Even hydrogen shows a cooling effect if its initial temperature is below -80°C .

(2) The drop in temperature is proportional to the difference in pressures on the two sides of the plug and increases as the difference in pressures becomes larger.

(3) This drop in temperature per atmosphere is larger for a low initial temperature; it decreases as the initial temperature of the gas is raised, and becomes zero for a certain value of the initial temperature, called the *Temperature of Inversion*. Above this temperature, which depends on the nature of the gas, a heating effect is observed.

The **Temperature of Inversion** is that temperature at which the Joule-Kelvin effect changes sign. Instead of showing a cooling on a drop in pressure, gases show a rise of temperature when their initial temperature is higher than the corresponding Temperature of Inversion. For a gas obeying the van der Waals' equation this temperature, T , is given by the relation

$$\frac{2a}{RT} = b. \quad (\text{See next Art.})$$

The temperature of inversion for air, oxygen and nitrogen lies above the room temperature. These gases will, therefore, be expected to show a cooling effect even at room-temperatures, when subjected to Joule-Kelvin process. This will not be so for hydrogen and helium which have their inversion temperatures very much below the room-temperature. In their case a slight heating may be expected if the experiment is performed at the room temperature.

The following table summarises the results obtained by Joule and Kelvin :—

Gas	Initial temp. of gas	Drop in temperature per atmosphere.
Air	0°C 50°C 93°C	.275°C .209°C .152°C
CO ₂	0°C 54°C 96°C	1.390°C .885°C .645°C
H	0°	.03°C (rise)

The fact that all gases (except Hydrogen above -80°C) show a cooling effect on free expansion proves the existence of inter-molecular attraction in all gases. This becomes most marked when the gases are near their points of liquefaction. It is, therefore, easy to see why the less permanent gases like carbon dioxide show so much departure from the ideal gas equation. The slight heating in the case of hydrogen is due to the fact that at ordinary temperatures the heating that results from the difference of the work done

on and by the gas more than compensates for any cooling due to inter-molecular attraction.

10.3. Theory of the Joule-Kelvin effect.

If V_1 and V_2 be the gram-molecular volumes of the gas on the high and low pressure side respectively, the net external work done by the gas in passing through the plug is $(p_2V_2 - p_1V_1)$. The work done by the gas in overcoming inter-molecular attraction is given by

$$\int_{V_1}^{V_2} \frac{a}{V^2} dV = \left(-\frac{a}{V_2} + \frac{a}{V_1} \right)$$

\therefore the attractive forces between the molecules are equivalent to an internal pressure of a/V^2 . (Art 8.6, van der Waals' equation)

Hence the work done by the gas against these forces is

$$p_2V_2 - p_1V_1 - \frac{a}{V_2} + \frac{a}{V_1} \dots \dots \dots (i)$$

and if there is to be no cooling, the equivalent amount of energy must be supplied to the gas.

Van der Waals' equation can be written approximately as

$$pV = RT - \frac{ap}{RT} + bp$$

Using this relation in (i) and also substituting the approximate value $\frac{RT}{p}$ for V in the terms $\frac{a}{V_1}$ and $\frac{a}{V_2}$,

(i) becomes

$$\begin{aligned} & \left[\left(RT - \frac{ap_2}{RT} + bp_2 \right) - \left(RT - \frac{ap_1}{RT} + bp_1 \right) - \frac{ap_2}{RT} + \frac{ap_1}{RT} \right] \\ &= \frac{a}{RT} (p_1 - p_2 + p_1 - p_2) - b(p_1 - p_2) \\ &= \left(\frac{2a}{RT} - b \right) (p_1 - p_2) \end{aligned} \quad (ii)$$

Relation (ii) gives the energy which must be supplied to compensate for the cooling.

Since $p_1 > p_2$, $(p_1 - p_2)$ is always positive. Heat supplied is positive, only if $\frac{2a}{RT} > b$ and if no heat be supplied a cooling will result. There will be no cooling if $\frac{2a}{RT} = b$. This equation gives the Temperature of Inversion, T .

If dT is the cooling produced, the heat which must be supplied to restore the original temperature is $C_p \cdot dT$, and

$$C_p \cdot dT = \left(\frac{2a}{RT} - b \right) (p_1 - p_2),$$

from which dT can be obtained.

The Van der waals' equation cannot, however, be used for a *quantitative calculation* of the Joule-Kelvin effect, or of the Temperature of Inversion. This is so because the van der Waals' equation does not represent even approximately a real gas *in the range of temperatures and pressures here involved*. Estimations of cooling can be made by using empirical formulae. Thus for the cooling produced in air, Hoxtons' formula

$$\mu = -\Delta T / \Delta p = 0.1975 - \frac{138}{T} + \frac{319p}{T^2},$$

where p is measured in atmospheres, gives good results between temperatures $0^\circ \rightarrow 280^\circ\text{C}$ and pressures $1 \rightarrow 220$ atmospheres.

QUESTIONS

1. (a) Give an account of the Joule-Kelvin experiment for determining inter-molecular attractions in gases.

What conclusions can be drawn from this experiment?

(b) How will you account for the heating effect observed in the case of hydrogen?

2. Obtain an expression for the cooling produced when a gas expands through a porous-plug.

3. Distinguish between Joule-Kelvin effect and adiabatic cooling. What advantage does a cotton-wool plug possess over a simple hole made in a plate?

4. Give a simple theory of the Joule-Kelvin effect.

Why has hydrogen a negative Joule-Kelvin coefficient?

Van Der Waals Equation
K. Theory of Gases
Porous plug Expt.
Platinum resistance thermometer
Sealed gas Equation

CHAPTER I

LIQUEFACTION OF GASES. PRODUCTION OF LOW TEMPERATURES

If you have built castles in the air, your work need not be lost; that is where they should be. Now put foundations under them.

—H. Thoreau

The mightiest works have been accomplished by men who have somehow kept their ability to dream great dreams.

—Bowie.

Historical. Liquefaction of gases started in 1823 when Faraday succeeded in liquefying chlorine, hydrogen sulphide, sulphur-dioxide, ammonia, hydrochloric acid gas etc. by highly compressing and simultaneously cooling them in freezing mixtures. He, however, failed to liquefy nitrogen, hydrogen, oxygen etc. in this way and therefore called them *permanent gases*.

An important advance was made in 1862, when Andrews showed that compression can result in liquefaction only if a gas is at or below its *critical temperature*. If this precaution be ignored, the compression of a gas, no matter how great, will not result in its liquefaction. He thus showed the great importance of the critical temperature. Oxygen was liquefied in 1877 by Pictet and Cailletet by the *Cascade Process*, in which the necessary preliminary cooling was produced in stages—the rapid evaporation of an easily liquefiable gas helping to liquefy a more difficult gas. Nitrogen was liquefied in 1883.

The method failed to liquefy hydrogen and helium because their critical temperatures are so low that the necessary initial cooling could not be produced by any known method. But then the Joule-Kelvin effect (discovered in 1853) proved a friend in need. A compressed gas when allowed to expand freely across a nozzle suffers a cooling in overcoming inter-molecular attractions between its molecules provided its initial temperature is below its *temperature of Inversion*. To obtain cooling at a faster rate, Claude made the expanding gas do external work in addition to overcoming inter-molecular attractions. Dewar obtained liquid hydrogen in 1895 and Onnes produced liquid helium in 1908 and thus the last gas had been liquefied. In 1926, Keesom was able to obtain solid helium also.

11.1 The liquefaction of chlorine by Faraday has already been

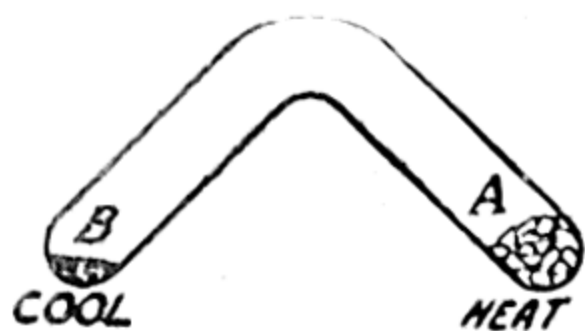


Fig. 11.1 Liquefaction of Chlorine

referred to. Crystals of chlorine hydrate were placed in the limb A of a stout Λ -shaped glass tube, which was then sealed. Chlorine was evolved in large quantities on heating A and developed a high pressure. The limb B was cooled in a freezing mixture, when the chlorine liquefied into an oily liquid. Following the line of attack indicated by Faraday some other gases were liquefied.

11.2. Carbon Dioxide. Thirlorier liquefied carbon dioxide, whose critical temperature is $+31^{\circ}\text{C}$ merely by subjecting it to a pressure of about 76 atmospheres. The gas was produced by dropping sulphuric acid on sodium bicarbonate contained in a stout copper cylinder lined with lead. The large volume of the gas evolved, collected in another cylinder joined to the first by means of a copper tube, where it liquefied under its own pressure. If the temperature rose above $+31^{\circ}\text{C}$ the cylinder was cooled by surrounding it with ice-cold water. The above method can be used for all gases whose critical temperatures are above the room temperature.

11.3. Liquefaction of Gases. The following are three important methods for liquefying gases :—

(1) **By cooling a gas below its critical temperature and applying a suitable pressure to it simultaneously.**—No initial cooling is necessary in the case of gases like carbon-dioxide and methyl chloride whose critical temperatures are above the ordinary room temperature. For the liquefaction of those gases whose critical temperatures are below the room temperature, the necessary cooling is produced in stages, *an easily liquefiable gas helping in the liquefaction of the more resistant gas*. An easy gas like methyl chloride is first liquefied. It is then made to evaporate rapidly by reducing the pressure on its surface, the latent heat being drawn from the liquid remaining behind. The temperature of the latter falls progressively. A coil containing a compressed gas which is rather more difficult to liquefy, is placed in this cooling liquid and when the temperature of this compressed gas falls below its critical temperature, it liquefies.

This is known as the **cascade process** and is due to Pictet. It is used for producing liquid oxygen, liquid air etc. However, all gases cannot be liquefied in this way.

(2) **By applying the Joule-Kelvin Effect.**—The compressed gas is first cooled below its Temperature of Inversion and is then made to expand across a nozzle. It uses a part of its own energy in overcoming the attractive forces which its molecules exert on one another and suffers a cooling thereby. This cooled gas is now made to flow round the in-coming gas which on expansion falls further down in temperature. This progressive cooling of the gas is continued till it ultimately liquefies. This is known as the **Principle of Regenerative Cooling** and has been used by Linde for obtaining liquid air and liquid hydrogen.

(3) **Claude's Process.**—Here the gas is allowed to expand adiabatically doing external work. It helps in driving the compressor and uses a part of its own energy in doing this. The rate of cooling of the gas is much greater because in addition to Joule-Kelvin cooling, the gas also suffers a loss of energy in doing external work. This cooled gas then flows round the gas which is now coming to work the compressor and produces a large initial cooling of this gas. After expansion this second lot of gas cools still more and so on. Liquefaction sets in at a very early stage. The first method failed to

liquefy hydrogen and helium because their critical temperatures (-240°C and -268°C respectively) are so low that the necessary initial cooling of the gases could not be produced.

The second method has the advantage that a much lesser preliminary cooling is necessary in this case. Thus hydrogen need only be cooled to -80°C , its temperature of inversion and not to -240°C , its critical temperature. The method can be worked into a continuous cycle. The rate of cooling is however, very slow in this case.

In the third method, the rate of cooling is very rapid. The greatest practical difficulty in this method was the un-availability of suitable lubricants for very low temperatures, but that has been overcome.

Nowadays, gases are being liquefied on a commercial scale and find diverse uses. In industry the last two methods only are being adopted. The first method is theoretically the best, in the sense that the least amount of work is required for the production of a unit amount of liquid, but it is cumbersome in practice and finds little use today.

Table of critical temperatures and pressures.

Gas	Critical Temperature	Critical Pressure
Air	-141°C	37 atmos
Carbon dioxide	31°	73
Chlorine	144°	76
Helium	-268°	2.3
Hydrogen	-240°	13
Nitrogen	-147°	33
Oxygen	-119°	50
Sulphur dioxide	157°	78

11.4. Pictet's Process for Liquid Oxygen.

For obtaining liquid oxygen we start with methyl chloride gas. Its critical temperature being 143°C , a mere compressive to 6 atmospheres suffices to liquefy it, the heat of compression is taken away by cold water circulating round *A*. The liquid methyl chloride is made to evaporate by reducing the pressure on its surface. The evaporation cools the remaining liquid and a temperature of -24°C is thereby reached. This cooled liquid circulates round a condenser *B* through which ethylene gas, critical temperature 10°C , is circulating under a pressure of 15 atmospheres. The cooling suffices to liquefy ethylene. By boiling ethylene liquid under a reduced pressure, a temperature of -169°C is reached, which is much lower than -118°C —the critical temperature for oxygen. The cooled liquid ethylene circulates round a condenser *C* through which oxygen under a pressure of 25 atmospheres is being passed. The cooling and compression succeed in producing liquid oxygen which can be stored in Dewar flask *F*.

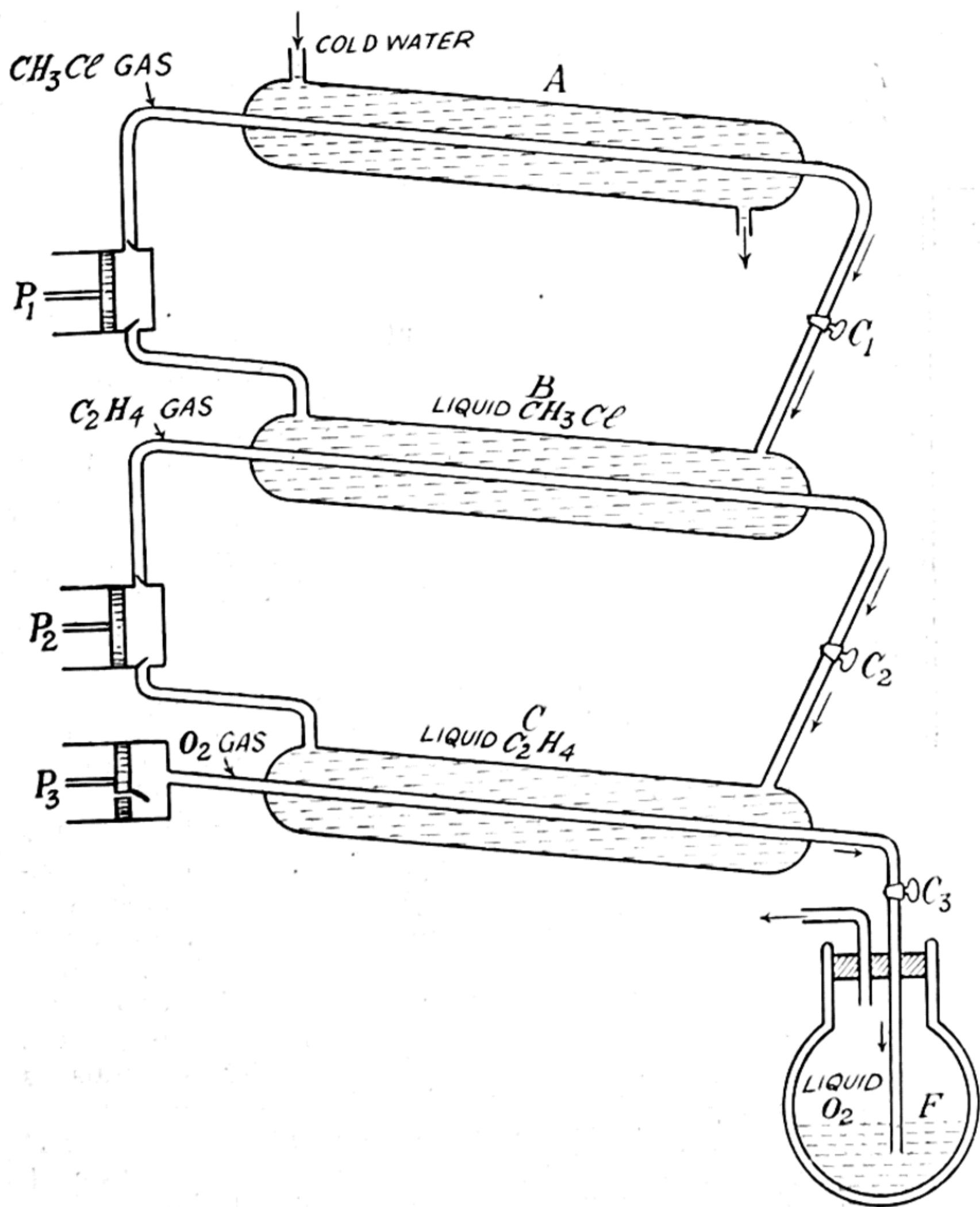


Fig. 11.2
Cascade process

The lowest temperature reached by the rapid evaporation of liquid oxygen is -218°C . Nitrogen with a critical temperature -147°C can be liquified by placing an additional condenser *D* below *C* (Fig. 11.2). At this stage the Cascade process stops.

11.5. Hampson's method for liquid air. Air, which has been freed from carbon-di-oxide and water vapours, enters at *A* and is compressed to a pressure of 150 atmospheres by the pump *P*. (Water vapour and carbon-di-oxide if present, will solidify at a very early stage and block the circulating system) Travelling down the copper spiral tube *B*, it escapes and expands at the nozzle *N* and suffers Joule-Kelvin cooling. Escaping at *N*, the cooled and expanded gas

moves up around B and cools the down-coming gas. In the actual arrangement B is a concentric spiral and the gas rises up in the annular space between the two spirals. This is the special feature of Hampson's device. Due to the progressive and regenerative cooling of the down-coming gas, liquefaction sets in after a few minutes of working.

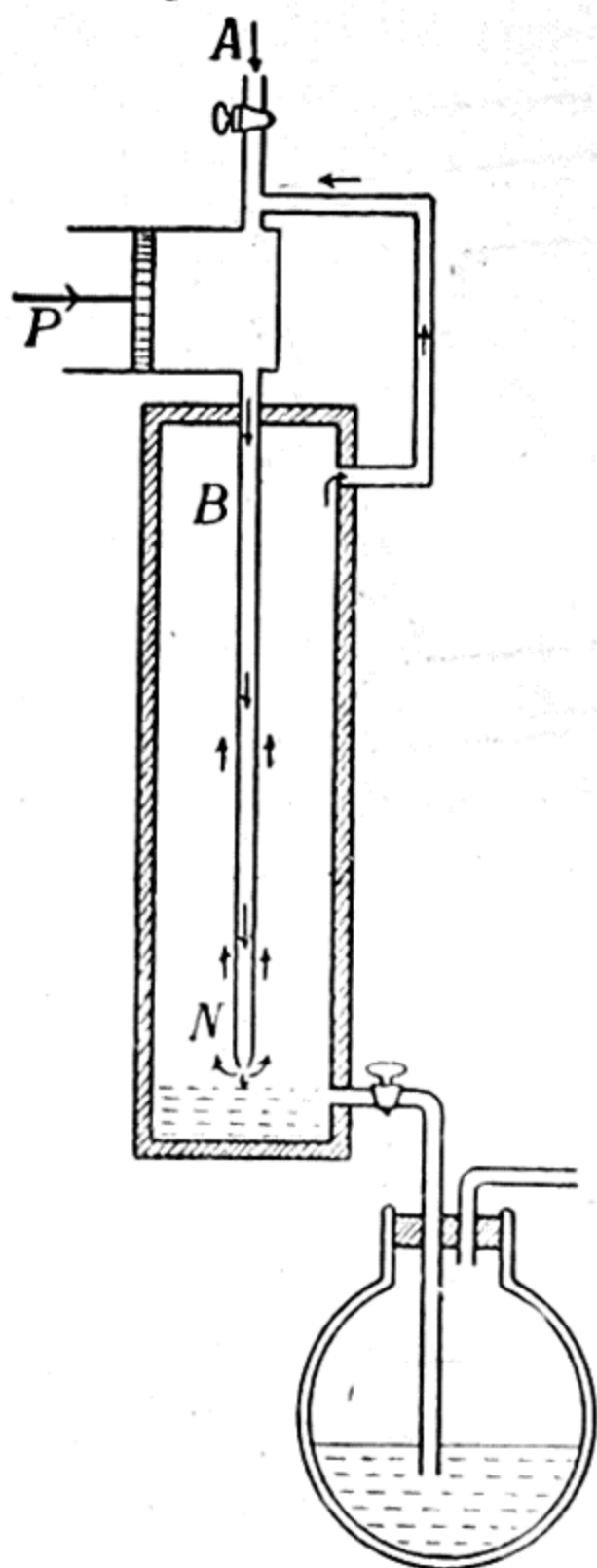


Fig. 11.4
Hampson's process.

pressed gas moving downwards and returns through the side-tube B into the *high pressure* system P_2 . When the down-coming gas in A has been sufficiently cooled, liquefaction sets in and the liquefied gas collects at C . Additional supplies of gas are drawn in through T , are compressed by P_1 to a pressure of 40 atmospheres and fed into P_2 to replace to fraction that has been liquefied.

By means of the pressure reducing valve R , the liquid is discharged into the chamber D from where it is fed into Dewar flasks and stored.

The advantage in the double system lies in the fact that *almost as much cooling* is produced by the expansion from 150 to 40 atmospheres as from an expansion from 150 to 1 atmosphere, while a much lesser amount of work has to be done in compressing most of the gas from 40 to 150 atmospheres (and a small fraction from 1 to 40 atmospheres) than if the *whole* gas had to be compressed from 1 to 150 atmospheres. This is a decisive gain from the commercial point of view.

The whole apparatus is very well lagged to prevent conduction of heat into it. The liquid is collected and stored in double-walled Dewar flasks.

11.5. Linde's process for liquid Hydrogen. The chief feature of the Linde's method is a combined low-pressure and high-pressure circulation. Pure hydrogen, free from carbon-di-oxide and water vapour, enters through the tap T and is compressed by the pump P_1 to a pressure of 40 atmospheres. Passing into P_2 it is compressed to 150 atmospheres and is circulated at that pressure. Its temperature is lowered much below -80°C (the inversion temperature for hydrogen) by the liquid-air condenser. The cooled and compressed gas enters the concentric system of copper spiral tubing at A . Moving down-wards, it suffers Joule-Kelvin cooling at the nozzle N and its pressure is reduced to 40 atmospheres. The cooled and expanded gas moving upwards through the annular space between the copper spirals, as in the Hampson's method, cools the com-

In the original method due to Dewar the whole of the gas was

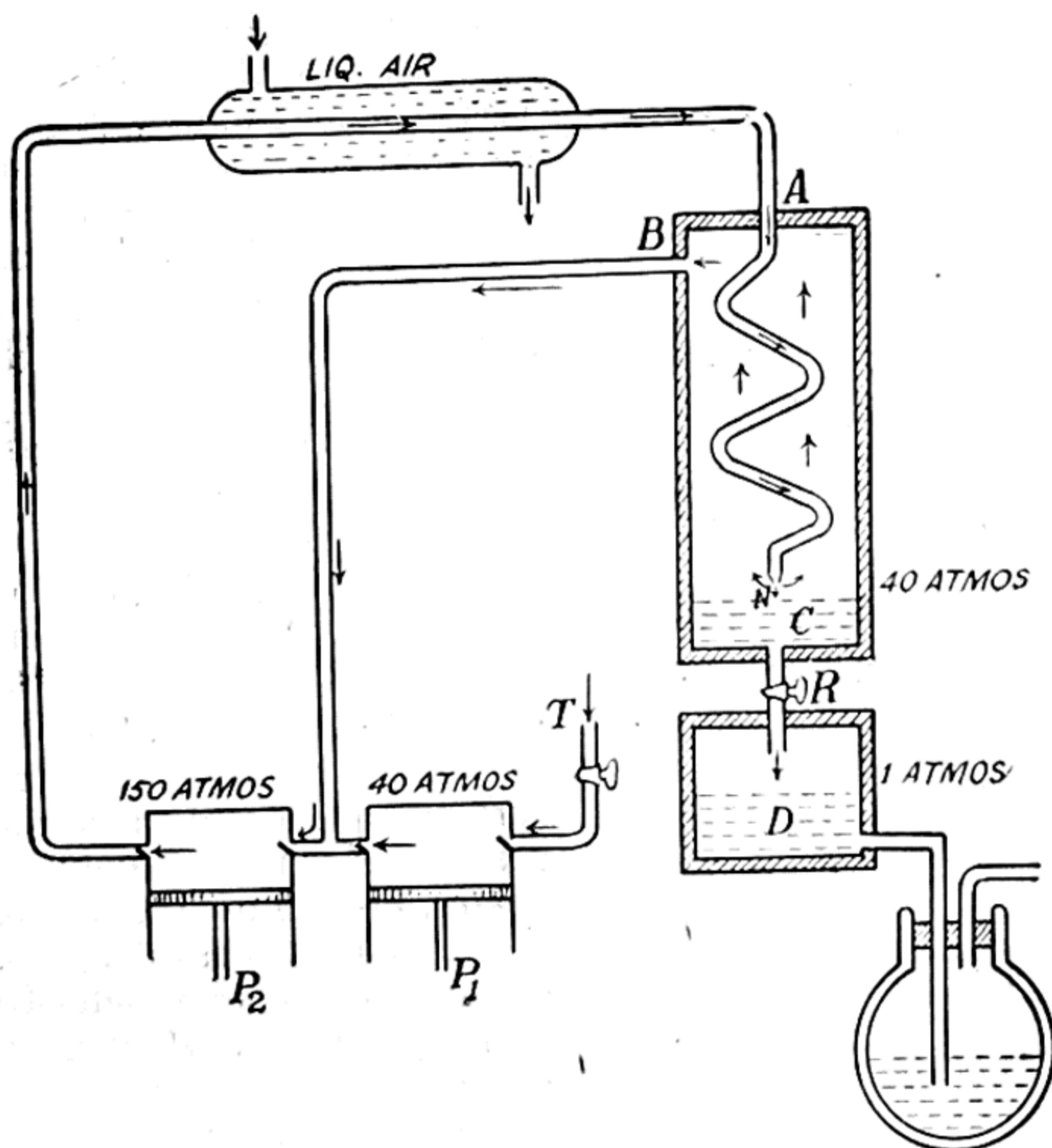


Fig. 11.4
Linde's process.

compressed from 1 to 150 atmospheres and the method was clearly more expensive than the one due to Linde.

By boiling liquid hydrogen under reduced pressure a white solid form of Hydrogen is obtained. This method has also been used for producing liquid air. In that case no precooling is necessary.

11.6 Claude's Process for liquid Air. Air, free from carbon-dioxide and water-vapour, is compressed in C. At A, the compressed air divides into two parts : one part constituting about 80% of the whole, goes to the expansion cylinder D where it expands adiabatically and suffers a cooling and as the air in D expands, the lever works the compressor and thus helps in driving it. The cooled air flows up at B into the Heat Exchanger and cools the compressed gas coming down A, the circulation of the air is continued and its temperature falls more and more till the critical temperature of air is reached when it liquefies and flows down into the vessel V. The gas flowing down A suffers Joule-Kelvin cooling as it expands through the nozzle. This gas also moves up through B to C as shown. The expanded air from D flows to C along B, E.

The chief difficulty encountered is that when the temperature of gas in *D* falls to a very low value, the lubricant solidifies and the piston is jammed. Petroleum ether and its mixture with vaseline have been used as lubricants and they work efficiently at these low temperatures. Once the gas has commenced to liquefy it serves as a lubricant itself.

The Claude process is only slightly more efficient than the Linde process and is mechanically much more complicated. For this reason the Linde process is usually preferred commercially.

By making the gas, cooled by the Claude process, to suffer Joule-Kelvin expansion, Kapitza has liquefied hydrogen and helium.

Kapitza has constructed a turbine-liquefier in which the initial pressure of the air is only 5 atmospheres, instead of 150 atmospheres in the Linde process. This is achieved by taking energy out of the gas by making it do work in the turbine, instead of depending on the Joule-Kelvin effect, which is of secondary magnitude. As the temperature of the air flowing through the turbine, unlike that of steam in steam turbine, is low, the working fluid is much more dense, being

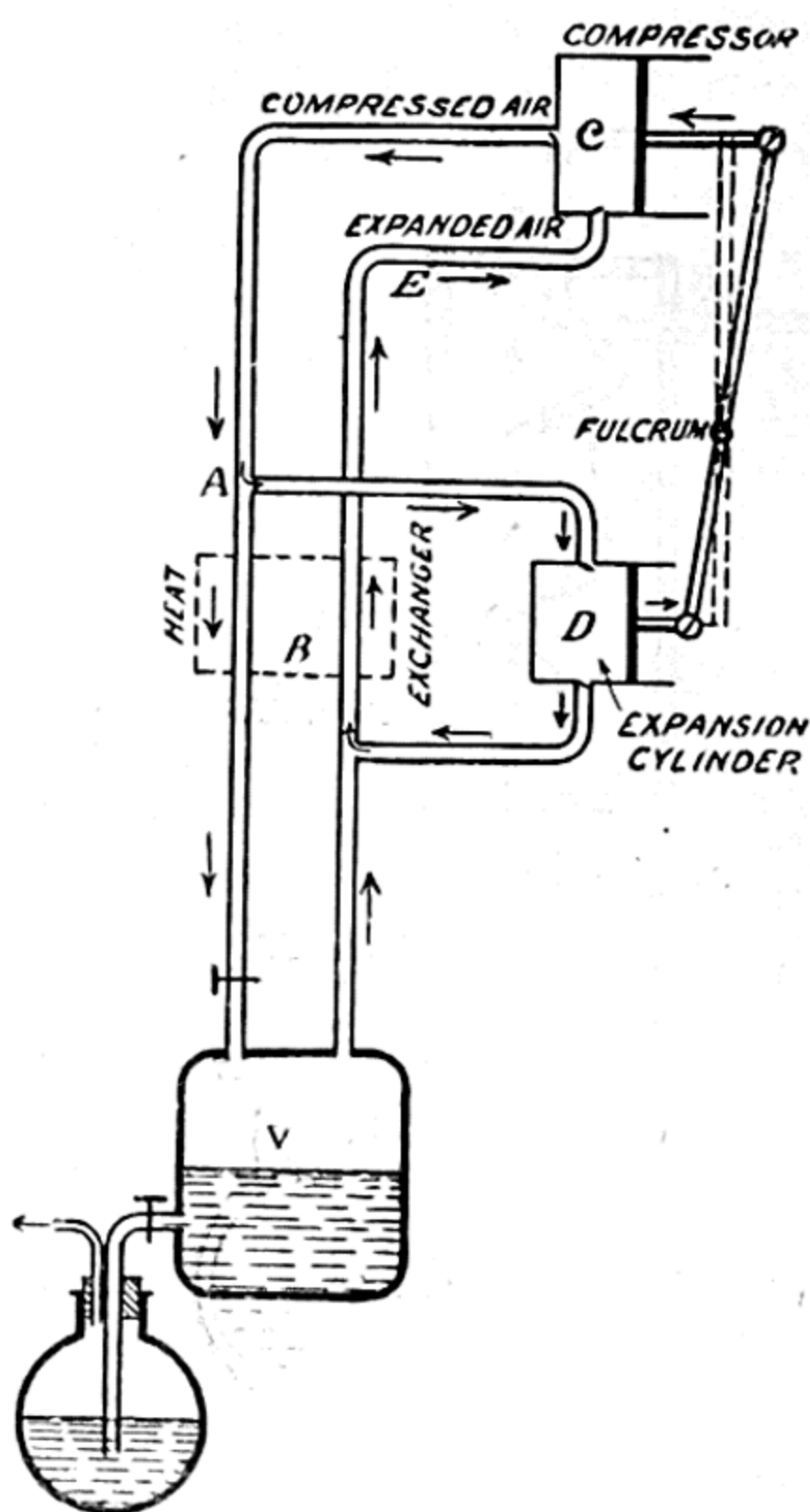


Fig. 11.5
Claude's Process.

about 5 times as dense as steam at 250°C . Consequently the turbine has to be designed to withstand considerable centrifugal forces, like a water-turbine. Air is compressed by a 50 H. P. compressor and after passing through water and air-coolers, is fed at about 7 atmospheres into the turbine. This runs at 40,000 revolutions per minute and develops about 4 H. P. The pressure of the air drops about 75 per cent in its passage through the turbine and if air enters at about -158°C , it emerges at about -187°C which is the boiling point of oxygen.

The apparatus produces about 50 kilograms of liquid air per hour and with minor improvements, would be as efficient as ordinary high-pressure liquefiers. It is compact owing to the absence of auxiliary equipment and it delivers liquid air within the short period of 20 minutes from starting.

11.7. K. Onne's method for liquid Helium. This was the last gas to be liquefied. Its liquefaction was accomplished by K. Onnes in 1908, in Leiden, by cooling the Helium gas to a temperature of

—258°C (its temperature of inversion is —240°C) by means of a bath of liquid hydrogen boiling under reduced pressure and then applying the Joule-Kelvin expansion to the cooled gas.

Gaseous Helium under a pressure of 36 atmospheres enters at *A* and then divides into two streams at *B*. The spirals *S*₁ and *S*₂ (shown straight in diagram) are cooled respectively by vapour of the hydrogen boiling under reduced pressure and cold helium gas. The two streams re-unite at *C* and again bifurcate. After suffering a cooling, as in the first case, they again mix at *D* and then undergo Joule-Kelvin expansion at the nozzle *E* and suffer a further cooling. The cooled helium gas then rises up and further cools the down-coming helium gas. At *S*, the rising helium gas is again compressed and fed into the main stream at *A*. When this cycle of operations has been performed a number of times, drops of liquid helium begin to trickle down at *E* and collect in the receiver from where the liquid can be drawn off.

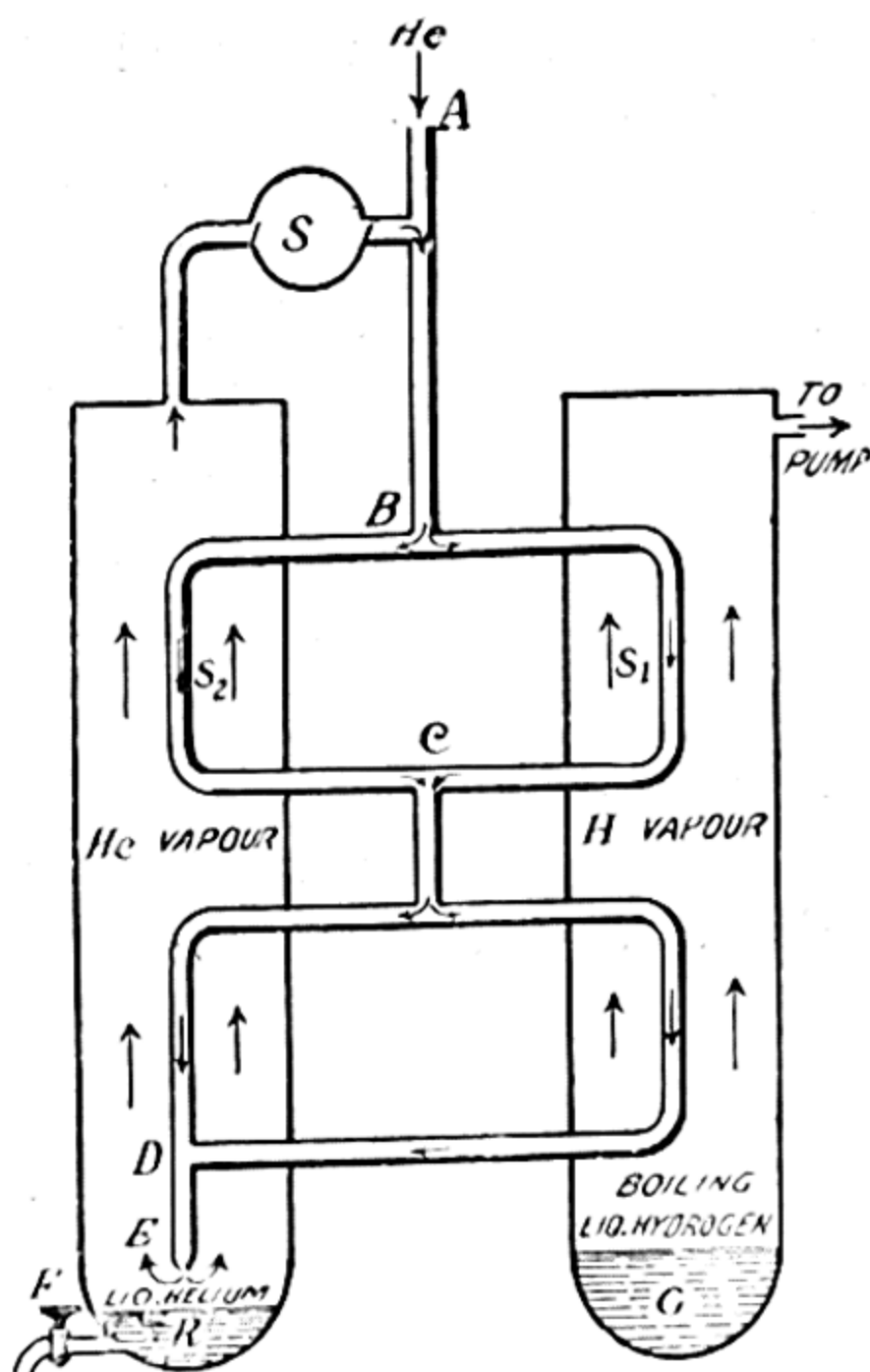


Fig. 11.6
Liquid Helium.

This intricate method of cooling is adopted because helium is a costly gas and with a limited supply at hand, it is worked round in cycles.

Kapitza has designed a liquefier which requires pre-cooling with liquid nitrogen only and the danger and inconvenience of using liquid hydrogen are avoided. The cooling upto the hydrogen temperature is obtained by allowing a part of the compressed helium to do external work as in the Claude process.

Onnes tried to produce solid helium by boiling the liquid under reduced pressure ; but the attempt failed. Though it sounds strange, solid helium can only be produced by subjecting the liquid to an external pressure. The solid Helium was obtained by Keesom in 1926.

11.8. Helium I and II. It has been found that below 2.19°K¹ the liquid helium which was contracting when cooled, now began to expand. A great change in its specific heat also occurs at this temperature. The liquid helium above 2.19°K is called *helium I* and that below it, is called *helium II*. The two liquid heliums differ

1. Temperatures measured from —273°C upwards are called °K (after Kelvin). Thus —240°C is 33°K and 0°C is 273°K

very much in their properties. Helium I is a normal liquid. Helium II has properties quite unlike those of any other substance—its heat conductivity is enormous, its internal friction is almost zero and it can flow easily through narrow capillaries. When it is forced through a capillary, the emerging liquid cools, while that which remains behind warms up.

If a light permanent bar-magnet be dropped into a Dewar flask containing a lead plate immersed in liquid helium, the magnet floats above the liquid and so to say, remains suspended some distance above the super-conducting lead. Occasionally it darts from side to side but does not come down. The approach of the magnet generates electric currents in the surface of the lead plate. The magnetic effect of these currents repels the magnet and keeps it floating.

Liquid helium behaves strangely when it is cooled below 2.19°K . If a vessel be lowered into it, the helium creeps in (i); when the vessel is lifted out of it, the liquid creeps out (ii); if the helium liquid is allowed to enter a narrow U-tube containing emery powder at the bottom of another vessel, it spurts from the tube at the top when light is thrown on the U-tube. This is due to absorption of energy by the powder, (iii).

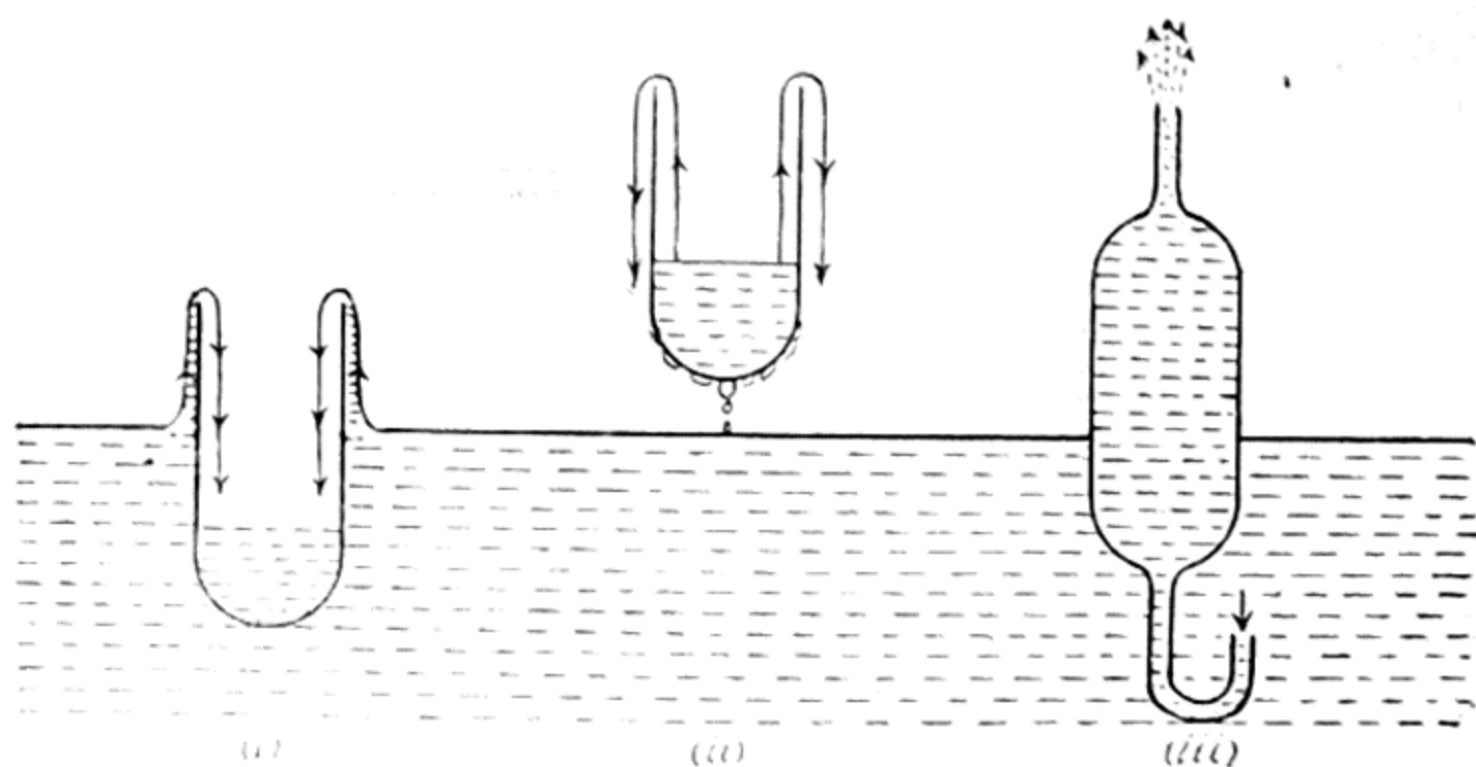


Fig. 11.7
Helium II

11.9 Production of Low Temperatures. About 150 years ago scientists began to realize that the temperature scale which they had established had a lower limit. While the scale appears to stretch into infinity so far as high temperatures are concerned (temperatures in the interior of stars are of the order of millions of degrees), the lower end is situated only 273°C below the melting point of ice. This is known as the **Absolute zero** of temperature.

Once it was known that a lower limit of temperatures existed, attempts were made to reach it. This march towards absolute zero makes a fascinating study and shows how much skill, patience, perseverance and hard labour has been put in by research workers.

Ice can reduce the temperature down to 0°C , but temperatures lower than 0°C can be produced by mixing certain salts with ice. While melting, the salt absorbs its latent heat and the heat of solution from the ice and the temperature of the mixture falls as a

consequence. This is the principle of *freezing mixtures*. Thus if to 100 parts of ice 33 parts of common salt be added, a temperature of -21.3°C is reached ; by adding 30 parts of calcium chloride, a temperature of -54.8°C is reached, while by using 32 parts of caustic potash -65°C can be reached.

The liquefaction of gases opened up a new line in the attainment of low temperatures. By boiling liquid sulphur-di-oxide under atmospheric pressure a temperature of -10°C is reached ; with boiling liquid methyl chloride -24°C is obtained ; ammonia gives -33.4°C and carbon-di-oxide -78.6°C , while with boiling liquid ethylene we can reach -103.7°C .

A great advance in low temperature production was made by Cailletet and Pictet in 1877 when they announced the liquefaction of oxygen. A temperature of -183°C or 90°K was thus reached. Liquid nitrogen boiling under normal pressure gives -195.8°C . Neon gives -246°C , hydrogen -252.78°C , while with helium -268.9°C is reached. By boiling helium under reduced pressure, a temperature of about 1°K was reached. Further progress then stopped.

In 1926 Giauque and Debye proposed the method of cooling by magnetic methods. Certain para-magnetic salts such as gadolinium sulphate, iron ammonium alum and potassium chromium alum contain in their molecules ions which behave as small magnets, having ordinarily a random distribution in direction even at low temperatures. If now a large magnetic field of 20,000—30,000 Gauss is applied, with the salt at an initial temperature of about 1°K , obtained by contact with a bath of liquid helium boiling under reduced pressure, the ionic magnets swing into line, producing a heating effect. This heat is taken up by the helium gas which surrounds the salt. The gas is then pumped out leaving the substance thermally insulated from its surroundings and the magnetic field is then switched off. The ions now try to regain their original orientations and therefore work has to be done by the substance. The necessary energy is obtained at the expense of the heat-energy of the salt itself, which therefore suffers a further fall in its temperature. Using this method de Haas and Wiersma at Leiden have reached 0.003°K .

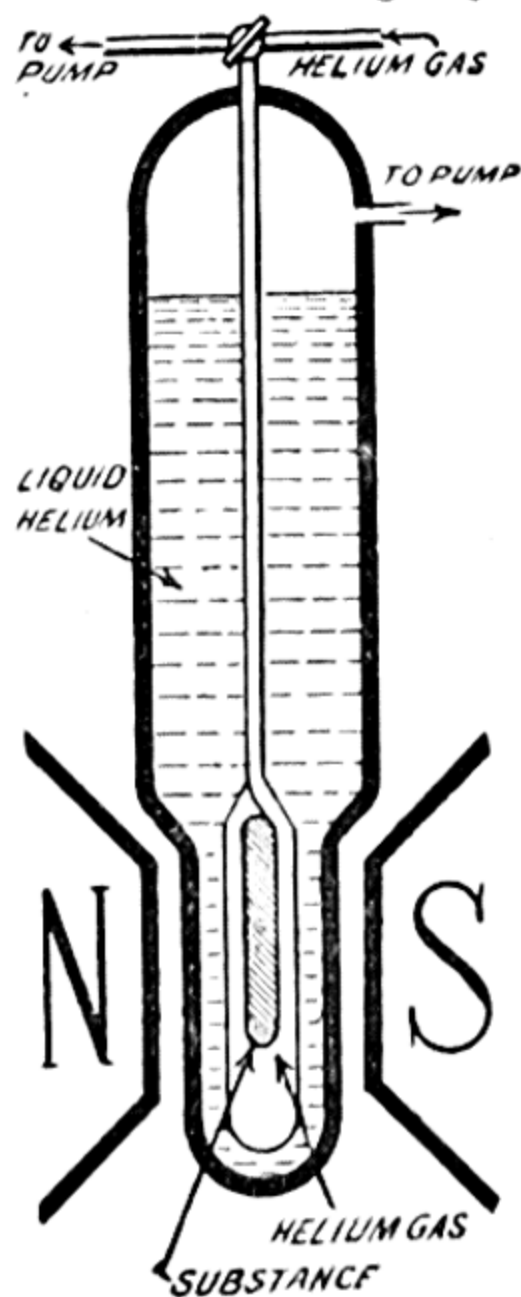


Fig. 11.8
Cooling by adiabatic demagnetisation

Attempts are being made to reach still lower temperatures. We may never be able to reach the Absolute Zero of temperature because according to the Third Law of Thermodynamics, while the Absolute Zero can be approached to any extent, it can never be

actually reached in practice. *"While Absolute Zero is a finite limit to our temperature scale, it has slipped into infinity so far as its experimental attainability is concerned."*

11.10. Measurement of Low Temperatures. A mercury thermometer cannot carry us beyond -39°C while with an alcohol thermometer we can reach -112°C . Although alcohol is less visible than mercury, it expands seven times as much for the same rise of temperature and is therefore superior to mercury in that sense. But then the liquid thermometers do not carry us very far.

Gas-thermometers are better. Dewar and others have shown that these thermometers can be depended upon down to the liquefaction point of the gas used. Temperatures down to -250°C can be measured using hydrogen and to -268°C using helium.

Resistance thermometers are much more convenient to use. Great care should, however, be taken in selecting the wire, which should be absolutely pure. Pure wires show a regular decrease of resistance with falling temperature but even a trace of impurity renders them unreliable. To determine temperatures below 80°K , the platinum thermometer is the most important instrument. A number of fixed points are available for calibration in this region.

Gas	Boiling point
Oxygen	90.20°K
Nitrogen	77.39
Neon	27.3
Hydrogen	20.42

Gold has also been used but possesses no special advantages. Both gold and platinum are unsuitable for very low temperatures because their resistance-temperature curves are so strongly curved that a large number of fixed points would be required to define the temperature curves. Lead also possesses certain advantages. Constantan and phosphor-bronze can be used for liquid helium temperatures.

Thermo-electric thermometers can also be used because a copper-constantan couple develops a large e. m. f. at very low temperatures. Couples of gold and silver or platinum and silver are also very sensitive. Thermo-couples are, however, not sensitive enough at these temperatures to serve as standards but are useful as control instruments.

Temperatures below 4°K are produced by a bath of liquid helium and are determined by measuring the vapour pressure of helium. Temperatures down to 1.5°K have thus been measured. For measuring still lower temperatures, the vapour pressure-temperature curve of helium has been extrapolated and temperatures upto 0.82°K have been measured.

Vapour pressure of liquid helium :—

Temperature °K	Vapour pressure in cm. of Hg.
4.899	132.90
4.219	76.00
3.218	25.00
2.298	5.00
1.538	0.50
1.055	0.025
0.899	0.0050
0.844	0.0025

Carbon resistance thermometers have been used for temperatures below 10°K , since the resistance of carbon *increases* very rapidly as the Absolute Zero is approached. Giauque (1938) has used both graphite rods (lead pencils) and strips of carbon ink as thermometers. These thermometers have the advantage that leads with fairly high electrical resistance and negligible thermal conductivity can be used.

The very low temperatures obtained by adiabatic demagnetisation have been estimated by measuring the magnetic susceptibility of the salt itself on the assumption that susceptibility varies inversely as the absolute temperature (Curies' Law).

11.11. Importance of Low-Temperature research. Very important work is being done at low temperatures. Specific heat determinations at low temperatures, the study of the properties of liquid helium and the study of the magnetic properties of substances at low temperatures are all of fundamental theoretical importance. Thus Keesom working in the region 1.7°K — 4°K has found that the specific heat of a substance is much greater than the value given by Debye's theory. The resistance of many substances has been found to decrease *suddenly* to very low values at very low temperatures. In fact, a whole subject of low-temperature physics has developed.

W. L. Bragg has observed that "Liquid helium is the starting-point for all work in the region within a degree or so of the Absolute Zero. The importance of investigation at this temperature is that the atoms have been robbed of almost all their thermal motion. In consequence, a whole new range of physical properties can be studied which are obscured by the irregular motion of the atoms at higher temperatures. Just as an anxious photographer tells his audience to keep quite still while he takes the cap off his camera, so the physicist likes the atoms to keep quiet while trying to discover some of their more delicate and small-scale properties."

11.12. Properties of substances at very low temperatures. With falling temperature the chemical activity of substances is greatly reduced. Dewar has shown that at -180°C , chemical reactions can no longer take place or at least the rate of chemical reaction is too

slow to be measured. Bacteria as well as many seeds retain their vitality even after prolonged cooling in liquid hydrogen. Again, at the temperature of liquid air, many substances like cotton, wool and egg-shells become faintly luminous. Many substances like lead which are not elastic at ordinary temperatures become so at the temperature of liquid air and a lead ball rebounds much higher than it would do at ordinary temperatures. On the other hand, rubber and iron become brittle, while tin disintegrates into a grey powder. K. Onnes tested the resistance of solidified mercury in a bath of liquid helium. Down to 4.3°K the resistance steadily decreased to about one-five hundredth of that at 0°C . Then the resistance dropped *suddenly* to less than one-millionth of the normal value *i.e., the mercury became supra-conducting*. Antimony, lead, aluminium etc., behave similarly. A current started by induction in a ring of the supra-conducting material continues to flow for days. Onnes supported a ring of lead in a liquid helium flask such that the ring was completely immersed in the liquid. The flask was supported in a magnetic field. By destroying the magnetic field a current was induced in the ring. The current persisted as long as the ring was in the liquid helium. The rate of decay was less than $1/40,000$ of its strength per hour. Hence the resistance of the ring must have been 10^{-12} ohms.

QUESTIONS

1. Discuss the production of cold by expansion of gases through porous plugs. How has this principle been applied in machines for liquefying air?

2. Give the Linde's method for liquefying gases. Discuss the principle on which it is based. What is the advantage of low and high pressure circulation.

3. Discuss and differentiate between the Cascade and Regenerative systems of producing low temperatures. How can these low temperatures be produced and measured?

4. Give the processes for liquefying carbon dioxide, oxygen and hydrogen. Why are different methods used in their liquefaction?

5. Give a method for producing liquid helium. Give the properties of liquid helium.

6. Write a historical note on the liquefaction of gases.

7. Write a note on the general methods of liquefaction of gases.

8. Describe the Hampson's method for producing liquid air.

9. Describe the Claude's process for obtaining liquid air.

Compare the various methods for liquefying gases. Which is the best method in your opinion.

10. Write an essay on the production of low temperatures.

11. Write a critical note on the measurement of low temperatures.

What is the importance of low-temperature research?

12. Briefly describe some of the properties of substances which are modified at very low temperatures.

CHAPTER XII

SECOND LAW OF THERMODYNAMICS

If you have an idea and it is a good idea, if you will only stick to it, you will come out all right.—*Rhodes*.

No hypothesis can lay claim to any value unless it assembles many phenomena under one concept.—*Goethe*.

12.1. Reversible and Irreversible Processes. A **reversible process** is one which can be retraced in the opposite order by an infinitely small change in the value of one of the factors controlling it. *i.e.*, when it is susceptible of occurring in either direction and a slight variation in the causes suffices to *reverse* the direction of the transformation. The working substance passes through exactly the same stages as in the direct process but the thermal and mechanical effects at each stage are exactly reversed. If heat is absorbed by the substance in the direct process it will be given out by it in the reverse process and if work is done by the substance in the direct process, work will be done on it in the reverse process. *There is absolutely no wastage of energy in reversible processes* and all energy that disappears is used up in doing mechanical work. All changes occurring reversibly must proceed infinitely slowly.

A vapour liquefies if heat is gradually abstracted from it but the same amount of heat will have to be supplied to the liquid to restore it to the original vaporous condition. The processes of liquefaction and evaporation are reversible. Again, when a gas is compressed, an amount of heat, equivalent to the work done on it, appears. If the compressed gas be now allowed to expand *slowly*, it will do external work (equal to that done on it) by absorbing a part of its own energy and will suffer a cooling thereby and the process is clearly reversible. If the expansion of the gas is violent, whirls and eddies will be formed and some of the work will be lost as heat and the change will not be exactly reversible. It is clear that reversible changes must take place infinitely slowly. The transference of heat from one body to another can be reversible only if the two bodies differ in temperature by an infinitesimal amount. In case of a finite temperature-difference, conduction and radiation occur which are not reversible. Strictly speaking reversible processes are only an ideal since frictional influences cannot be avoided in practice. Nevertheless, there are many real processes which are conducted at so slow a rate that they can be regarded as reversible within the limits of experimental error. *Rigorous reversibility is an ideal limit, while irreversibility is the rule.*

Irreversible Processes are those which cannot be retraced in the opposite order by reversing the controlling factors. Friction is irreversible. Heat is produced when a body moves against a resistance but

heat is again produced (and not absorbed) when the direction of motion of the body is reversed. Similarly, the Joule-Kelvin effect is irreversible—fall of temperature occurs whether a gas crosses the plug in one direction or in the reverse direction. Electric resistance is also irreversible. Heat is produced when a current crosses a conductor and is still produced (and not absorbed) when the direction of the current is reversed. *Joule-heating is irreversible while Peltier-heating is reversible.*

12.2. Conditions of Reversibility. (1) The substance undergoing a reversible change must not lose heat in overcoming friction, or by conduction or radiation. No heat should be transformed into electrical or magnetic energy.

(2) The changes in the pressure and the volume of the working substance must take place infinitely slowly so that when the substance is gaining heat its temperature differs infinitesimally from the hotter body and when it is losing heat it differs infinitesimally from the colder body.

12.3. Second Law of Thermodynamics. The First Law of Thermodynamics established an equivalence between the quantity of heat used up and its mechanical output, or vice versa. Joule, however did not specify the conditions under which a body can use its heat energy to produce a supply of work. This gap has been bridged by the Second Law of Thermodynamics which lays down the rule according to which work can be obtained by using the energy of a hot body. In fact, *the law is concerned with the direction in which energy transfers take place.* Work cannot be derived from heat unless this heat is allowed to fall from a higher to a lower level.

The heat engine—which is a device for getting mechanical work from heat—works by absorbing heat from a hot body. It converts some of the heat thus absorbed into mechanical work and rejects the rest to a body at a lower temperature. The steam which enters the cylinder of a steam engine from its boiler is hotter than the steam which is rejected by the cylinder to the atmosphere. The heat lost by the steam is used up in rotating the various parts of the machine. The mechanical energy delivered by the engine is due to the flow of heat from a higher to a lower temperature. If the boiler and the atmosphere were at the *same* temperature, no heat-flow would occur and no heat would be transformed into mechanical energy. The heat would be entirely unavailable. But a flow of heat would generate work only if it were properly harnessed, as in the steam engine.

As the engine absorbs more and more heat from the hot body, the latter suffers a progressive fall in its temperature. To get a *continuous* supply of work, the temperature of the hot body must be maintained constant. If this precaution be ignored, the hot body will ultimately become as cool as its surroundings. No further transference of heat will then be possible, the engine will stop working and no mechanical work will be obtained. Such considerations led Lord Kelvin to the conclusion that

'It is impossible to get a continuous supply of work by cooling a body to a temperature lower than that of the coldest of its surroundings.'

Again, in the case of a refrigerator—a machine for the artificial production of cold—heat is absorbed from a body at a lower temperature and rejected to a body at a higher temperature. Thus, in the ammonia-ice-machine, liquid ammonia absorbs its latent heat from a brine tank (whose temperature therefore falls) and turns into gaseous ammonia. The gaseous ammonia then enters a cylinder where it is compressed by a compressor. The compressed ammonia, then enters a coil immersed in a tank of cold water where it loses its own heat and the heat produced in it by compression, liquefies and is again ready for the next cycle.

We find that heat is being absorbed from the cool brine tank and is being rejected to water which is at a higher temperature, but heat is not flowing of itself from the colder to the hotter body. We have to employ an outside agency (the compressor in the present case) to make this transference possible. Considerations such as these led Clausius to conclude that

'It is impossible to cause heat to flow from a colder to a hotter body without absorbing energy from some external source.'

Of course, heat does not and cannot flow directly from a lower to a higher temperature. An intermediary absorbs the heat from the cold body and then passes it on to the hot body.

Both these are enunciations of the Second Law of Thermodynamics and are different ways of looking at the same problem. It can easily be shown that violation of the conditions imposed by the first form of the law also means a violation of its second form. Thus, suppose it is possible to get a continuous supply of work by cooling a body to a temperature lower than its surroundings. The working substance (say steam) will ultimately be absorbing heat from a cold body, converting some of it into work and rejecting the rest of the heat to a body at a higher temperature. This violates the Clausius form of the law.

Again, suppose it is possible to make heat flow of itself from a colder to a hotter body, say into a vessel of water. Steam will ultimately be formed, whose expansive force can be made to do external work. As the process is continued, the cold body will ultimately become cooler than its surroundings and will still be supplying work. This violates the Kelvin form of the law.

Hence both the enunciations of the law are equivalent to each other. This is one of the most important laws of Physical Science and finds the widest application but, like all other great laws, it cannot be directly proved.

It must be clearly understood that **the second law applies to reversible cyclic operations only**, i.e., to those reversible operations in which the substance ends in the same condition as regards its temperature, pressure, etc. as it started. Water evaporating from a vessel is cooled below the temperature of its surroundings (because the

vapour is all the time absorbing its latent heat from the water remaining behind) and work can be obtained from the escaping vapour. There is, however, no violation of the Second Law because no cycle of operations is being performed in this case.

12.4. Carnot Reversible Engine.—Imagine a cylinder with perfectly conducting bottom but with perfect non-conducting sides, containing the working substance (which may be anything) and closed with a perfectly non-conducting, frictionless, movable lid.

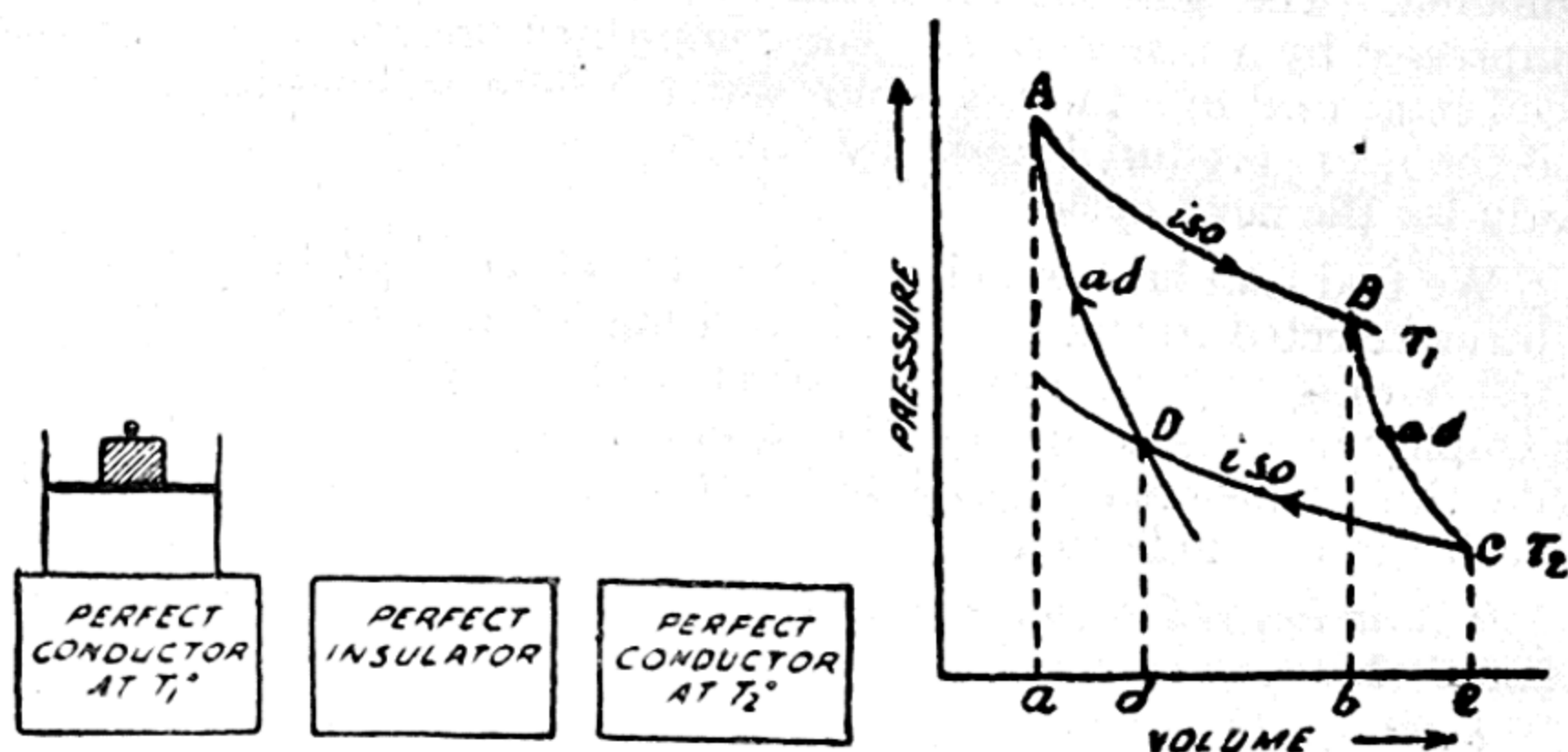


Fig. 12.4
Carnot's Engine.

Suppose the cylinder is placed on a perfectly conducting surface of infinite thermal capacity, whose temperature, T_1 , does not alter when any finite amount of heat is taken from it. Let A represent the initial pressure and volume of the substance.

(1) The weight on the lid is *slightly* decreased so that the substance expands *isothermally* to the condition represented by B , absorbing an amount of heat H_1 . Since the substance expands from v_A , the volume corresponding to A to v_B corresponding to B against an external pressure, an amount of work equal to the area of the figure $AabB$ will be done. The heat absorbed from the conducting surface is partly used up in doing this external work and partly in producing a change in the internal energy of the substance. This latter quantity depends upon the pressure, volume and temperature of the substance and since the pressure and volume at A and B are different, so is the internal energy of the substance. Internal energy is *independent* of the path by which the substance moves from one state to the other.

(2) The cylinder is now placed on a perfect insulator of heat and the substance is allowed to expand *adiabatically* by slightly diminishing the load on the lid again. Since the process is adiabatic the substance uses a part of its own energy in doing work against external pressure, and consequently its temperature falls. Suppose when the condition of the substance corresponds to the point C , its temperature is T_2 . In expanding from B to C it has done an amount of work represented by the area of the figure $BbcC$.

(3) The cylinder is now placed on a perfectly conducting surface at a temperature T_2 and having infinite thermal capacity. The load on the lid is now increased so that the substance undergoes a slow *isothermal* compression at a temperature T_2 till its condition is represented by a suitable point D . The heat H_2 generated by the compression will be conducted away by the surface and the temperature of the substance will be maintained at T_2 throughout. During this compression an amount of work represented by the area $CcdD$ will be done *on* the substance.

(4) The cylinder is put back on the insulator again, the load on the lid is increased so that the substance undergoes a slow *adiabatic* compression. The heat generated by the compression will gradually raise the temperature of the substance. The compression is stopped when the pressure and volume of the substance correspond to the point A again. Its temperature will also be T_1 and consequently *its internal energy will be the same as at the beginning of the process*. An amount of work represented by $DdaA$ will be done *on* it, in the process. The substance is said to have performed a Carnot cycle. [The point D is to be such that after the adiabatic compression the substance ends in the condition A . This point D can be determined by a preliminary experiment by allowing the substance to *expand* adiabatically from its condition A .]

During the above cycle of operations, the substance absorbs an amount of heat H_1 from the hot body and rejects H_2 to the cold body. The net gain of heat is $H_1 - H_2$. At the same time an amount of work represented by the area

$$ABCD (= AabB + BbcC - CcdD - DdaA)$$

is done by it. Since there is no change in the internal energy of the substance, $H_1 - H_2$ is mechanically equivalent to the work done by it.

The Carnot cycle is perfectly reversible and can be *exactly* retraced in the opposite order. An amount of heat $H_1 - H_2$ will then be evolved and an amount of work represented by the area $ABCD$ will be absorbed, *i.e.*, the engine will work as a refrigerator.

12.5. The Carnot engine cannot be realized in practice because in all actual engines a part of the energy is always lost in overcoming friction. It nevertheless, gives us an idea of an ideally simple engine. It is the standard with which the performance of all actual engines is compared, because.

(1) It is perfectly reversible in its action and reversibility eliminates all waste.

(2) All heat is gained by it at the temperature of the hot body only, and rejected at the temperature of the cold body. In an actual engine, the temperature of the hot body, progressively falls as it gives out heat and that of the cold body rises as heat passes into it. Such engines, therefore, do not make as full a use of the heat, which they draw, as the Carnot engine does, or in other words: 'They do not make full use of the available temperature-difference.'

The efficiency of an engine which is the ratio of the heat spent in doing external work, W , to the total heat drawn from the hot body in one cycle, is given by

$$E = \frac{W}{H_1} = \frac{H_1 - H_2}{H_1} = 1 - \frac{H_2}{H_1} = 1 - \frac{T_2}{T_1} \text{ (See art. 12.8b)}$$

It is clear that out of the total heat absorbed by the engine, only a fraction $\left(1 - \frac{T_2}{T_1}\right)$ is available for work. The fraction $\left(1 - \frac{T_2}{T_1}\right)$ is called the *Available Energy*, while the fraction $\frac{T_2}{T_1}$ is *unavailable*. Thus if the hot body is at 100°C or 373°A and the cold body is at 0°C or 273°A , the available energy is only $1 - \frac{273}{373} = \frac{1}{4}$ approximately, while the remaining $\frac{3}{4}$ is unavailable. It will be seen that *even under ideal conditions, only the available energy (and not the whole heat energy supplied to the engine) is converted into work.*

12.6. Carnot engine has maximum efficiency. *All reversible engines working between the same two temperatures have the same efficiency irrespective of the amounts of heat which they draw from their respective sources and no engine can be more efficient than a Carnot engine working between the same temperature limits. This is also known as **Carnot's theorem**.*

If possible, suppose an engine P has a greater efficiency than a Carnot engine Q working between the same two temperatures. It means $\frac{W_1}{H_1} > \frac{W_2}{H_2}$ where H_1 and H_2 are the amounts of heats absorbed by the two engines from their sources and W_1 and W_2 the amounts of work done by the two respectively. If they perform equal amounts of work, $W_1 = W_2$; hence $H_2 > H_1$; *i.e.*, for doing equal amounts of work P draws less energy from its source than Q does.

Arrange the two engines in such a way that when P works normally, it drives Q backwards (Fig. 12.2). Suppose

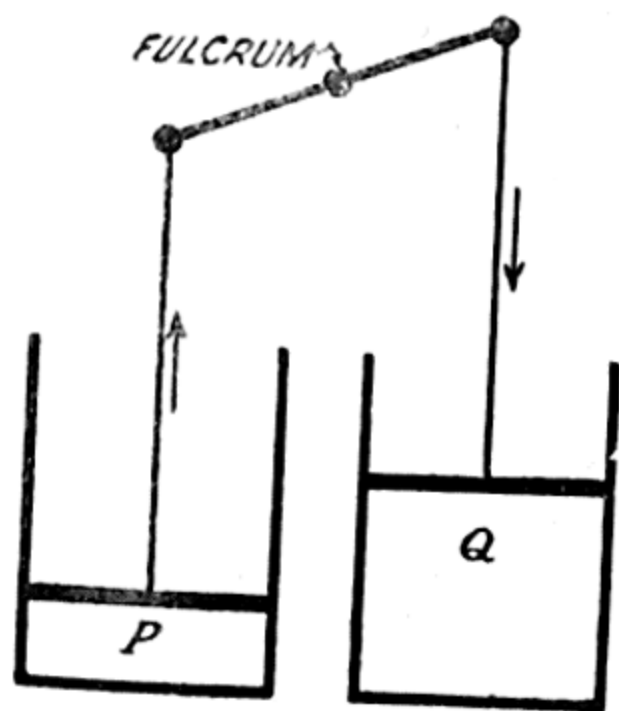


Fig. 12.2
Coupled Carnot Engine.

both the engines use the same hot and cold bodies. P will draw H_1 heat from the hot body and perform W_1 work while Q will reject H_2 heat to the hot body and absorb W_2 work. The net result will be that an amount of heat $H_2 - H_1$ will be transferred to the hot body by this coupled system while the external work done is $W_1 - W_2 = 0$. This heat $H_2 - H_1$ must therefore come from the cold body. The two engines constituting together a self-acting engine would thus transfer heat from a refrigerator to a hot source or that, heat will flow from a cold to a hot body without the expenditure of any work which

is impossible because it violates the Second law. Hence the two engines must be equally efficient. Since in every actual engine there is a waste of energy, it will be less efficient than a Carnot engine working between the same limits of temperature.

The efficiency of a Carnot engine, therefore, depends only on the two temperatures between which it works. It neither depends on the amount of heat drawn by the engine from its source nor on the nature of the working substance used. It follows that no engine can be more efficient than a Carnot engine, which, therefore, possesses the maximum efficiency for given temperature limits.

Again, the essential condition for reversibility is that all changes—*isothermal or adiabatic*—must take place infinitely slowly. This means that although the Carnot engine is the most efficient, it will take an infinite amount of time to perform any specific amount of work. Its actual rate of working, *i.e.* its power, will therefore be zero. Hence a Carnot engine possesses maximum efficiency but zero power.

12.7. Work Scale of Temperature. Those properties of matter which vary continuously with heating have been used for the measurement of temperatures. The various thermometers depend upon the particular property of matter used in their construction and are expected to agree only at the fixed points; *marked deviations are observed at other temperatures.* The gas thermometer shows a superiority in the sense that it depends upon the property of no one gas in particular.

With the idea of constructing a temperature scale which should be independent of the properties of *all* substances, Kelvin (at the suggestion of Joule) made Carnot engine the basis of a scale of temperature measurements. We have seen that the *efficiency of the Carnot engine depends only on the two temperatures between which it works and on nothing else, i.e.,* the efficiency is some function of the temperatures θ_1, θ_2 .

$$\text{or} \quad \text{Eff.} = 1 - \frac{H_2}{H_1} = \phi(\theta_1, \theta_2)$$

$$\text{or} \quad \frac{H_1}{H_2} = \frac{1}{1 - \phi(\theta_1, \theta_2)} = f(\theta_1, \theta_2) \quad \dots (i)$$

Kelvin proposed that the ratio between the heats received and rejected by a Carnot engine, working between the temperature limits θ_1 and θ_2 , is the same as between the two temperatures themselves. He thus adopted the simplest form of equation (i). Hence

$$\frac{H_1}{H_2} = \frac{\theta_1}{\theta_2}.$$

The justification for the above simplifying assumption can be seen from the following: For engines A, B and C working between the temperatures $\theta_1 - \theta_2$, $\theta_2 - \theta_3$, and $\theta_1 - \theta_3$ respectively we have

$$(a) \quad \frac{H_1}{H_2} = \frac{\theta_1}{\theta_2}, \quad (b) \quad \frac{H_2}{H_3} = \frac{\theta_2}{\theta_3}, \quad (c) \quad \frac{H_1}{H_3} = \frac{\theta_1}{\theta_3}.$$

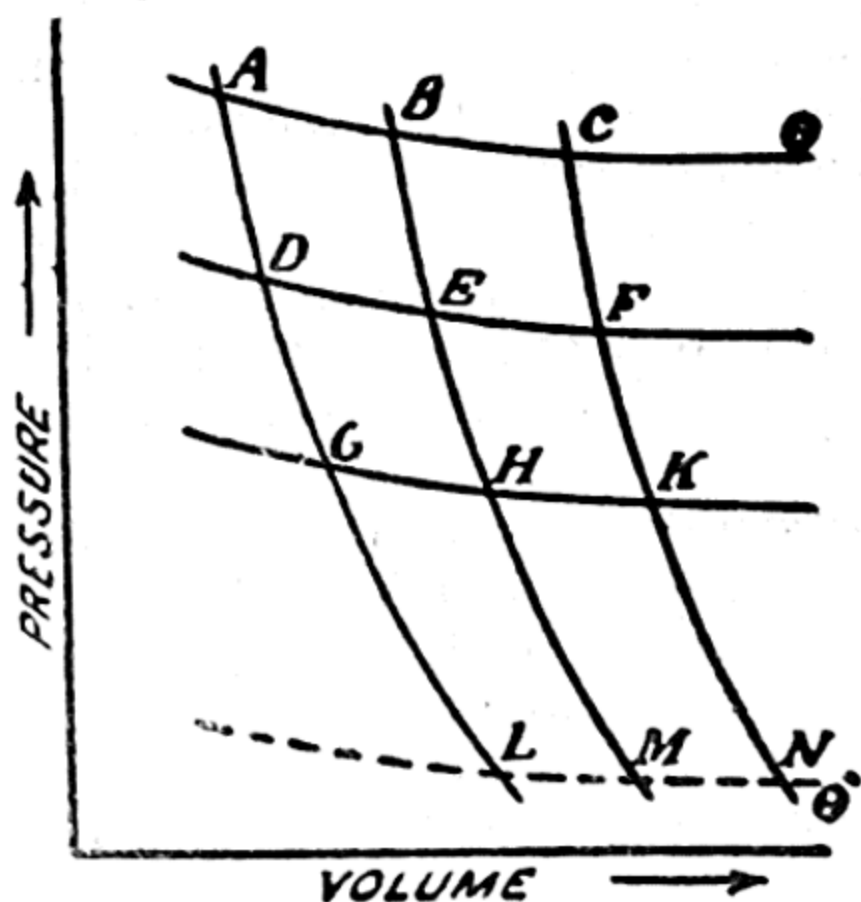
If now A and B be so coupled that the cold body of A is the hot body of B , B will absorb as much heat from it as A rejects to it. The cold body of A therefore plays no practical part and we are left essentially with an engine that absorbs H_1 heat from the hot body of A at θ_1 and rejects H_3 heat to the cold body of B at temperature θ_3 . Hence for this coupled system, $\frac{H_1}{H_3} = \frac{\theta_1}{\theta_3}$ which is the same as (c) above.

If the interval between the ice and steam points be divided into 100 equal parts and θ_0 be the ice point,

$$\frac{H_{\text{steam}}}{H_{\text{ice}}} = \frac{\theta_0 + 100}{\theta_0},$$

whence θ_0 can be calculated and a temperature scale constructed.

This is the Work scale or the Thermodynamic scale of temperatures. It has the maximum theoretical support, but is not capable of being realised in actual practice because reversibility is impossible to achieve in any actual machine. This is its greatest drawback.



Graphical representation of work scale. Let ABC be an isothermal line for any temperature θ , the point A corresponding to the initial state of the working substance and the points B and C to its condition when H and $2H$ heat has been added to it respectively. Let LMN be the isothermal for $\theta = 0$ or θ_0 .

Draw the adiabats AL , BM and CN through the points A , B and C . The areas $ALMB$ and $BMNC$ are equal, because each represents the work done by a perfect engine that draws H heat at θ and

converts the whole of it into work and itself falls to the temperature of Absolute zero. Draw $(\theta - 1)$ isothermals between θ and θ_0 , dividing the areas $ALMB$ and $BMNC$ into θ equal parts. Then the absolute scale of temperature is represented by these isothermals. Incidentally this shows a correspondence between the Work scale and the Absolute gas scale which we now seek to determine independently.

12.8. Work Scale and Absolute Gas Scale. Temperatures measured on the Work scale agree with those measured on the Absolute gas scale.

Suppose a Carnot engine contains a unit mass of an *ideal gas* as the working substance. The temperature limits between which the engine works are θ_1 and θ_2 on the work scale and T_1 and T_2 on the gas scale.

By the definition of work scale

$$\frac{H_1}{H_2} = \frac{\theta_1}{\theta_2} \quad \dots \quad \dots \quad (a)$$

Suppose the gas absorbs H_1 heat in expanding isothermally from A to B at a temperature T_1 . Work done by it in expansion is

$$\int_{V_A}^{V_B} p dv = rT_1 \int_{V_A}^{V_B} \frac{dv}{V} \quad (\because pV = rT_1)$$

$$\text{or } H_1 = rT_1 \log_e \frac{V_B}{V_A}$$

Similarly, work done on the gas in moving along the isothermal T_2 from C to D is

$$- \int_{V_C}^{V_D} p dv = -rT_2 \int_{V_C}^{V_D} \frac{dv}{V}$$

and if H_2 is the heat liberated

$$H_2 = rT_2 \log_e \frac{V_C}{V_D}$$

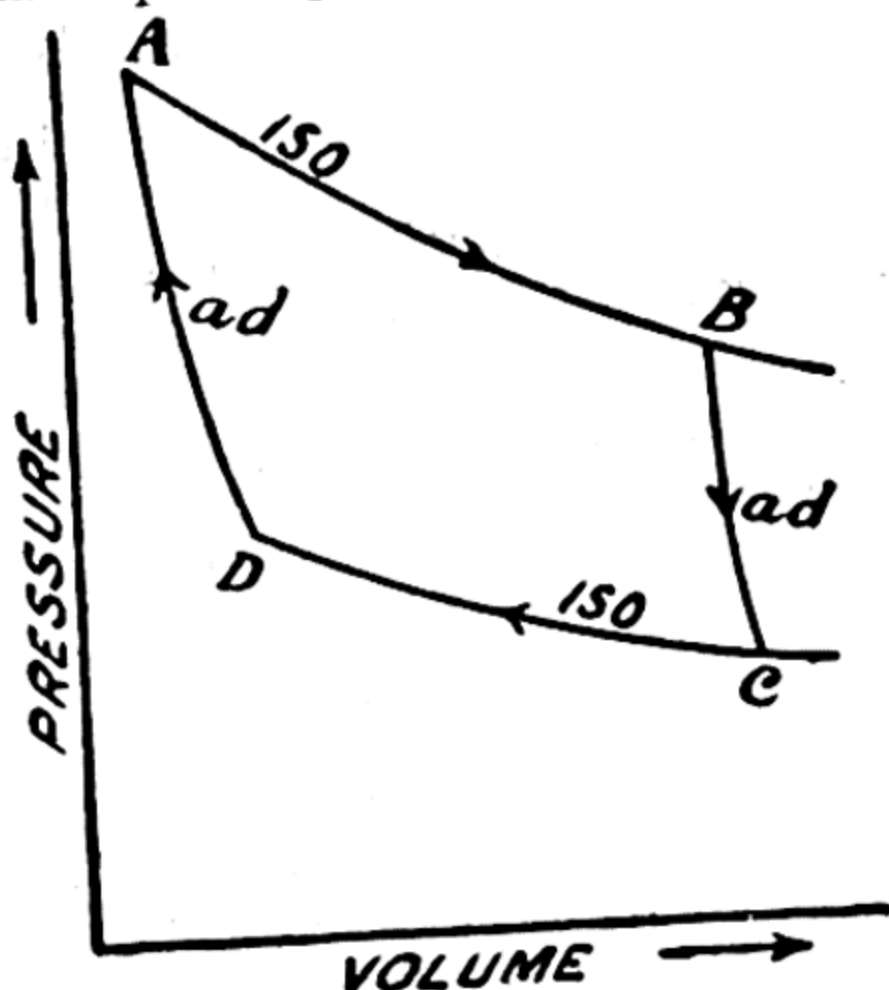


Fig. 12.4
Carnot Cycle

$$\therefore \frac{H_1}{H_2} = \frac{rT_1 \log_e \frac{V_B}{V_A}}{rT_2 \log_e \frac{V_C}{V_D}} \quad \dots \quad \dots \quad (i)$$

Since A and B lie on the same isothermal,

$$p_A V_A = p_B V_B \quad \text{or} \quad \frac{p_A}{p_B} = \frac{V_B}{V_A} \quad \dots \quad (ii)$$

$$\text{Similarly} \quad \frac{p_D}{p_C} = \frac{V_C}{V_D} \quad \dots \quad \dots \quad (iii)$$

Again, since A and D lie on the same adiabatic

$$p_A V_A^\gamma = p_D V_D^\gamma \quad \text{or} \quad \frac{p_A}{p_D} = \left(\frac{V_D}{V_A} \right)^\gamma \quad \dots \quad (iv)$$

$$\text{Similarly} \quad \frac{p_B}{p_C} = \left(\frac{V_C}{V_B} \right)^\gamma \quad \dots \quad (v)$$

Dividing (iv) by (v)

$$\frac{p_A}{p_B} \cdot \frac{p_C}{p_D} = \left(\frac{V_B}{V_A} \cdot \frac{V_D}{V_C} \right)^\gamma \quad \dots \quad (vi)$$

Using (ii) and (iii) in (vi),

$$\frac{V_B}{V_A} \cdot \frac{V_D}{V_C} = \left(\frac{V_B}{V_A} \cdot \frac{V_D}{V_C} \right)^\gamma$$

Or,

$$\left(\frac{V_B}{V_A} \cdot \frac{V_D}{V_C} \right)^{\gamma-1} = 1$$

or
$$\frac{V_B}{V_A} \cdot \frac{V_D}{V_C} = 1, \text{ or } \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

which, when substituted in (i), gives

$$\frac{H_1}{H_2} = \frac{T_1}{T_2} \quad (\text{by (a) above}) \quad \dots (vii)$$

Hence

$$\frac{T_1}{T_2} = \frac{\theta_1}{\theta_2} \quad \dots (viii)$$

(1) If in (viii) $T_1 = 0$, θ_1 also becomes zero, or the zeros of the two scales are identical.

(2) Again if there be 100 degrees between the ice and steam points, and if T_0 and θ_0 be the values of the ice point on the two scales.

$$\frac{100 + T_0}{T_0} = \frac{100 + \theta_0}{\theta_0}$$

or

$$T_0 = \theta_0$$

or the ice point is the same on the two scales.

(3) Now put $T_2 = T_0$ and $\theta_2 = \theta_0$ in (viii) and let $T_1 = T$, where T is any temperature on the gas scale and if θ be the corresponding temperature on the work scale we have

$$\frac{T}{T_0} = \frac{\theta}{\theta_0}$$

i.e., corresponding temperatures on the two scales are the same, or the two scales are identical.

(b) Efficiency of a Carnot engine is given by the relation $E = 1 - \frac{H_2}{H_1}$.

To prove that it is also equal to $1 - \frac{T_2}{T_1}$, proceed, as above and prove that $\frac{H_2}{H_1} = \frac{T_2}{T_1}$. The required result follows immediately.

12.9. Clapeyron's Latent Heat Equation.

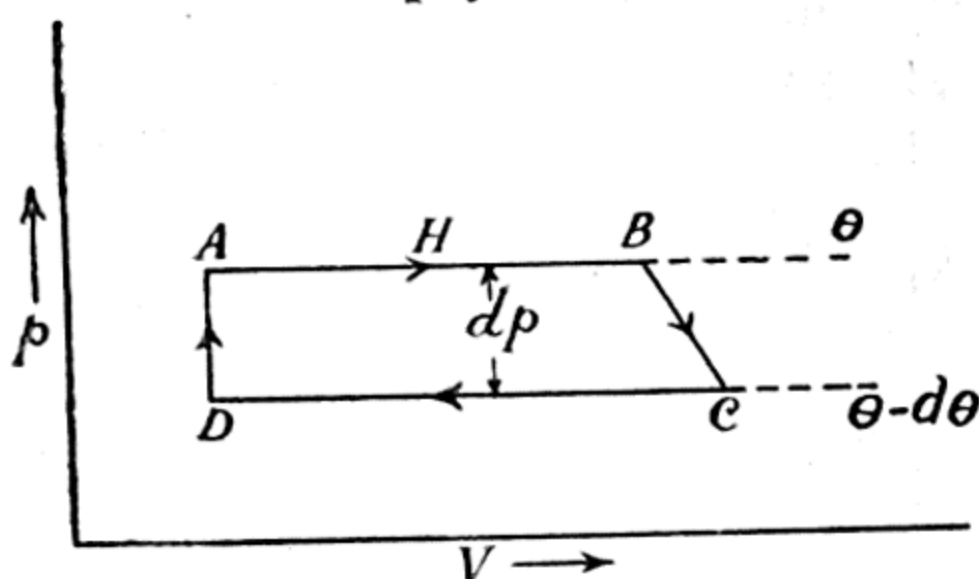


Fig. 12.5

Clapeyron's equation

Consider a Carnot engine with one gm. of a liquid as the working substance. Let the initial condition of the working substance be represented by the point A (Fig. 12.5), so that its volume is v_1 , temperature is θ while its pressure is just below the saturation pressure of the liquid for temperature θ . The liquid will begin to evaporate and when the whole of it has evaporated,

it will have a volume v_2 corresponding to B. An amount of heat $H = L$, the latent heat of the liquid at θ , will be absorbed in the process. Having reached B, reduce the pressure on the vapour by dp ,

it will expand and cool down to $(\theta - d\theta)$ till C is reached. If pressure be maintained at this new value, the gas will start condensing till it is completely liquefied at D , an amount of heat $(H - dH)$ equal to the latent heat corresponding to the temperature $(\theta - d\theta)$ will be liberated. Restore the pressure to the original value, thus completing the cycle. And the cycle is clearly reversible. Hence II law of Thermodynamics can be applied.

$$\therefore \frac{H - dH}{H} = \frac{\theta - d\theta}{\theta}$$

$$\text{or} \quad \frac{dH}{H} = \frac{d\theta}{\theta} \quad \dots (i)$$

Now $dH = dw = dp (v_2 - v_1) =$ the area $ABCD$ and $H = L$, the latent heat, hence

$$\frac{dp(v_2 - v_1)}{L} = \frac{d\theta}{\theta}$$

$$\text{or} \quad \frac{dp}{d\theta} = \frac{L}{\theta(v_2 - v_1)} \quad \dots (ii)$$

which is the **Clapeyron's Equation**.

(1) For an evaporating liquid, its gaseous volume v_2 , is greater than the liquid volume v_1 , hence $(v_2 - v_1)$ is always positive. As L and θ are $+ve$, $dp/d\theta$ is also $+ve$, or vapour pressure of a liquid increases as its temperature rises and vice versa.

(2) In the case of melting ice v_2 , the volume of water formed is less than v_1 , the volume of ice taken or $(v_2 - v_1)$ is $-ve$. Therefore $dp/d\theta$ is $-ve$ or the melting point of the ice is lowered when the pressure acting on it is increased.

12.10. Example 1. Calculate the volume of a gram of steam at 100°C . Given : latent heat of water at $100^\circ\text{C} = 535$ calories ; change of Boiling point with pressure 0.37°C per cm. of mercury ; density of mercury 13.6 and acceleration due to gravity $= 980 \text{ cm./sec}^2$.

$$\frac{d\theta}{dp} = 0.37^\circ\text{C} ; \text{ or } \frac{dp}{d\theta} = \frac{1}{0.37}, \theta = 100 + 273 = 373.$$

$$L = 535 \times 4.2 \times 10^7 \text{ ergs}$$

$$1 \text{ atmosphere} = 76 \times 13.6 \times 980 \text{ dynes/sq. cm.} = 1.013 \times 10^6 \text{ dynes/sq. cm.}$$

$$\frac{L}{\theta(v_2 - v_1)} = \frac{535 \times 4.2 \times 10^7}{373(v_2 - v_1)} \text{ dynes/sq. cm./degree}$$

$$= \frac{535 \times 4.2 \times 10^7}{373(v_2 - v_1)} \times \frac{76}{1.013 \times 10^6} \text{ cm. of Hg/}^\circ\text{C}$$

$$\text{or} \quad \frac{1}{0.37} = \frac{535 \times 4.2 \times 10^7}{373(v_2 - v_1)} \times \frac{76}{1.013 \times 10^6}$$

$$\therefore (v_2 - v_1) = 1661$$

$$\text{or} \quad v_2 = 1661 + 1 = 1662 \text{ c.c.}$$

[\therefore volume of one gm. of water $= v_1 = 1$ c.c.]

Example 2. Determine the decrease in the melting point of ice for each atmosphere rise of pressure. Given : Latent heat of ice $= 80$ cal; $J = 4.2 \times 10^7$ ergs/cal ; volume of one gm. of ice $= 1.091$ c.c.

Required $\frac{d\theta}{dp}$

$$\frac{d\theta}{dp} = \frac{\theta(v_2 - v_1)}{L}$$

$$= \frac{273(1 - 1.091)}{80 \times 4.2 \times 10^7} \text{ degrees per dyne per sq. cm.} \quad \dots(i)$$

The decrease of M. P. per atmosphere will be 1.013×10^6 ($= 76 \times 13.6 \times 980$) times (i)

$$= \frac{273 \times (-.091) \times 1.013 \times 10^6}{80 \times 4.2 \times 10^7}$$

$$= -0.0075^\circ\text{C}$$

12.11. Entropy.—The conception of entropy is very important in the study of the behaviour of heat engines.

According to the Kelvin's scale of temperature, the ratio between the quantities of heat H_1 and H_2 received and rejected respectively by a reversible Carnot engine working between the temperature limits θ_1 and θ_2 is given by the relation

$$\frac{H_1}{H_2} = \frac{\theta_1}{\theta_2} \quad \text{or} \quad \frac{H_1}{\theta_1} = \frac{H_2}{\theta_2}$$

This shows that whenever a substance moves between two adiabatics

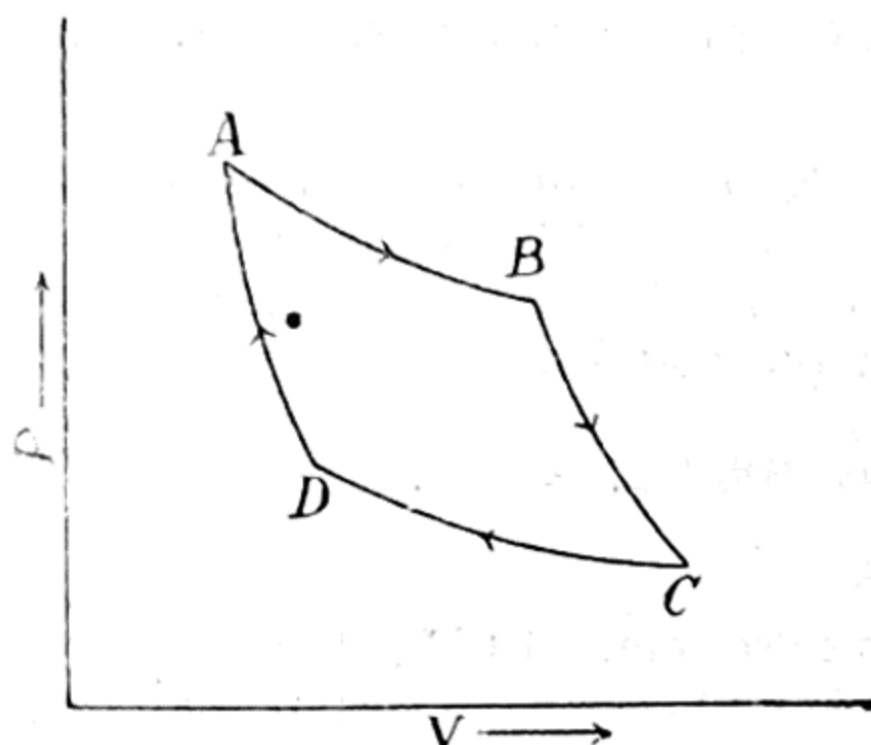


Fig. 12.6
Entropy

AD and BC , along any isothermal path, provided the path is reversible, the quantity $H/\theta = \phi$ remains constant. This is called the *Difference of Entropy* between the two adiabatics. Since no gain or loss of heat takes place when a body moves along a (reversible) adiabatic path, all points on the same adiabatic have the same entropy. When, however, a body moves from one adiabatic to another along an isothermal path a change of entropy does occur but this is independent of the isothermal

path taken, provided it is reversible. Hence **Entropy** is that quantity which remains constant during a reversible adiabatic process. It is thus a definite function of the state of a body and is not in any way affected by the manner in which that particular state has been realized. We, however, cannot measure the absolute value of the entropy of a substance in any given state. We can only measure changes of entropy that result from a change of state of a body.

Since H_1 is heat *absorbed* while H_2 is the heat *rejected*, they have opposite signs, or

$$\frac{H_1}{\theta_1} = -\frac{H_2}{\theta_2}, \text{ or } \frac{H_1}{\theta_1} + \frac{H_2}{\theta_2} = 0.$$

i.e., the change of entropy in any reversible cycle is zero.

This is true not only for the Carnot cycle, but for any cyclic operation, provided it is exactly reversible. This can be shown by sub-dividing the cycle into elementary Carnot cycles by means of very close adiabatics. In the limit AB and CD will coincide with the isothermals (shown dotted) and may themselves be considered isothermals. If dH_1 is the heat absorbed along AB at temperature θ_1 and dH_2 the heat rejected along CD at temperature θ_2 we have for the elementary Carnot cycle $ABCD$

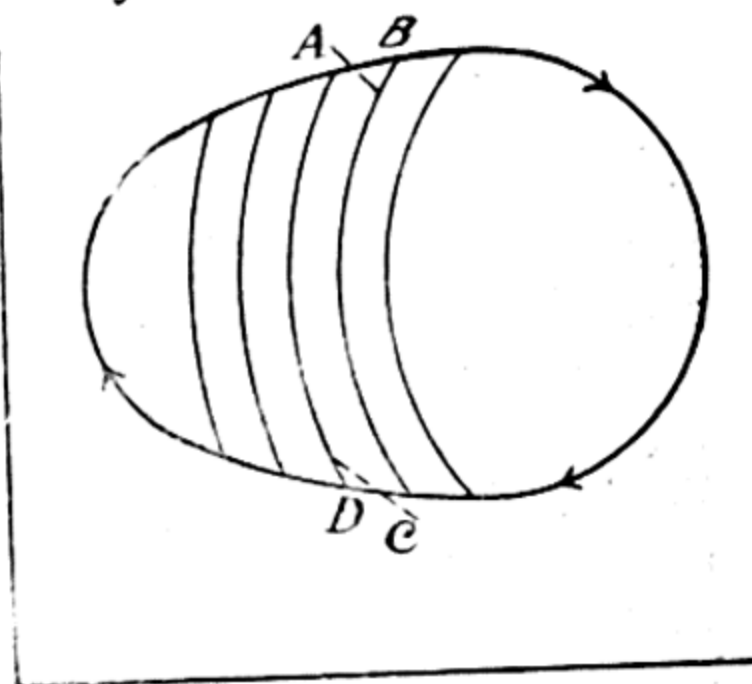


Fig. 12.7
Reversible cycle

$$\frac{dH_1}{\theta_1} + \frac{dH_2}{\theta_2} = 0$$

Summing up for all the elementary cycles,

$$\Sigma \left(\frac{dH_1}{\theta_1} + \frac{dH_2}{\theta_2} \right) = 0$$

or

$$\int \frac{dH}{\theta} = 0$$

the integration extending over the whole area.

Calling

$$\frac{dH}{\theta} = d\phi.$$

we have,

$$\int d\phi = 0$$

or the change of entropy in the reversible cycle is zero.

To bring out the real importance of entropy it must be emphasized that while the heat absorbed or rejected by a substance depends upon the reversible changes that it undergoes, entropy is independent of these and is defined solely by its initial and final conditions. Entropy is, therefore, a definite physical entity and is as good in defining the state of a substance as are its pressure or volume.

12.12. We can look at entropy from another angle. Let us supply an amount of heat dH to a substance, and let its temperature rise by θ degrees. Generally, equal additions of heat will produce equal increments in temperature, unless an internal change in structure also takes place. In the later case, there will be no rise in temperature till the change is complete. Proceeding thus we can plot the thermal history of the substance; we have simply to note the value of

$$d\phi = \frac{dH}{\theta}$$

at each step ;

and

$$\phi = \int \frac{dH}{\theta}$$

is the *total* change in entropy. If we start with a substance with its initial temperature in the neighbourhood of absolute zero, and give it small equal doses of heat dH , and note the rise of temperature T at each step, we will have before us an entropy-chart showing all the changes that the substance has undergone along with the temperature at which each change has occurred. When $T \rightarrow 0$, $\phi \rightarrow \infty$ and there is a discontinuous rise in entropy. Such a discontinuity always indicates the occurrence of phase-change, like melting, or else a transformation of the crystal structure.

A solid (*e.g.*, crystal, in which the particles are regularly spaced) must be heated at constant temperature to change its state to a liquid. This change is accompanied by a destruction of the ordered arrangement of the molecules. There is also an increase of entropy because heat has been given to the body at a constant temperature θ . θ remaining constant, dH has increased, hence also the entropy dH/θ . Similarly a change from the liquid to the gaseous state is a move towards perfect chaos and this is also attended by an increase in the entropy of the substance. The importance of entropy is thus evident. It provides us with a method by which we can watch the internal developments in the substance, from outside. According to Boltzmann the *entropy* of a substance is a measure of the degree of disorder prevailing among its molecules, just as temperature is the measure of the degree of hotness of a substance. Entropy is as real as the temperature and is, perhaps, more important. According to the III law of Thermodynamics, all substances are in a state of perfect *order* at Absolute zero of temperature and their entropy is therefore zero.

12.13. Entropy of an ideal gas. We have seen that

$$dH = dU + dW \quad \dots \quad (i)$$

Also $d\phi = \frac{dH}{T}$ or $dH = Td\phi$. (putting T for θ)

and (i) gives

$$Td\phi = dU + dW \quad \dots \quad (ii)$$

For an ideal gas, $dU = Cv.dT$ and $dW = p.dv$ for one gram of the gas. Hence (ii) is transformed to

$$Td\phi = Cv.dT + p.dv$$

or

$$d\phi = C \left(\frac{dT}{T} + \frac{p}{T} dv \right)$$

But $pv = rT$

$$\therefore d\phi = Cv \frac{dT}{T} + r \frac{dv}{v}$$

Integrating, $\int_{\phi_0}^{\phi} d\phi = Cv \int_{T_0}^T \frac{dT}{T} + r \int_{v_0}^v \frac{dv}{v}$

$$\begin{aligned} \text{or } \varphi - \varphi_0 &= Cv [\log T - \log T_0] + r [\log v - \log v_0] \quad \dots \dots (iii) \\ \text{or } \varphi &= Cv \log T + r \log v + \text{constant} \end{aligned}$$

Example. Calculate the change in the entropy of 1 gm. of nitrogen when its temperature rises from 50° to 100° while its volume increases four-fold, given that $Cv = 0.18$ and molecular weight = 28.

$$\begin{aligned} \text{From (iii), } \varphi - \varphi_0 &= Cv \log_e \frac{T}{T_0} + r \log_e \frac{v}{v_0} \\ &= 0.18 \log_e \frac{373}{323} + \frac{1}{28} \cdot \frac{8.31 \times 10^7}{4.18 \times 10^7} \log_e \frac{4}{1} \\ &= 0.18 - 2.3026 \left[\log_{10} \frac{373}{323} + \frac{1.986}{28} \log_{10} 4 \right] \\ &= 0.58 \text{ cal/degree.} \end{aligned}$$

12.14. Entropy tends to a maximum. We have seen that in a reversible cyclic operation, the change of entropy is zero, but reversibility cannot be achieved in actual physical operations. When a substance is undergoing cyclic operations, it will be losing energy in irreversible processes like friction, conduction, radiation, etc., tending to lower its temperature. Hence in actual practice.

$$\frac{H_1}{\theta_1} \neq \frac{H_2}{\theta_2}.$$

because θ_2 is less than its ideal value θ'_2 if no heat losses had occurred,

$$\therefore \frac{H_2}{\theta_2} > \frac{H_2}{\theta'_2}$$

and $\frac{H_1}{\theta_1} + \frac{H_2}{\theta'_2}$, will be a positive quantity which will go on increasing as cycle after cycle is performed. Hence, although in an ideally reversible operation the change of entropy is zero, in actual operations entropy will go on increasing, tending to a maximum value.

It is interesting to remark here that all physical operations tend towards establishing an equality of temperatures between various bodies. A state of stagnation will ultimately be reached when, due to impossibility of transference of heat, all work would be impossible. Differences of temperature and pressure will even out, all motion will cease as a result of frictional influences and the universe will die of inanition. In terms of entropy, the total entropy of the universe will increase to a maximum value and then proceed no further. Stagnation then appears to be the ultimate destiny of the physical universe!

12.15 Example 1. Calculate the change of entropy when 100 grams of water at 30°C are mixed with 200 grams of water at 0°C , assuming that the sp. heat of water is 1 cal/gram at all temperatures.

Let T be the final temperature, then

$$\begin{aligned} 100(30 - T) &= 200(T - 0), \\ T &= 10^\circ\text{C} \end{aligned}$$

or

$$\text{Now } dH = m.s.d\theta = 100 \times 1 \times d\theta = 100d\theta$$

$$(i) \text{ Decrease of entropy} = \int_{30+273}^{10+273} \frac{100 d\theta}{\theta}$$

$$\log_{10} 303 = 2.48144 \quad] = 100 [\log_e 283 - \log_e 303]$$

$$\log_{10} 283 = 2.45179 \quad \} = 100 \times 2.3 [\log_{10} 283 - \log_{10} 303]$$

$$\log_{10} 273 = 2.43616 \quad] = -230 \times 0.02965$$

$$= -6.82$$

$$(ii) \text{ Increase of entropy} = \int_{273}^{283} \frac{200 d\theta}{\theta}$$

$$= 200 \times 2.3 [\log_{10} 283 - \log_{10} 273]$$

$$= 460 \times 0.01563$$

$$= 7.19$$

$$\therefore \text{ Increase of entropy} = 7.19 - 6.82$$

$$= 0.37 \text{ units.}$$

Example 2. 10 gms of steam at 100°C pass into 100 gm. of water at 15°C . Calculate the change of entropy. [Latent heat of steam = 536 calories.]

Let θ be the final temperature, then

$$10 \times L + 10(100 - \theta) = 100(\theta - 15)$$

or

$$10 \times 536 + 1000 - 10\theta = 100\theta - 1500$$

or

$$\theta = 71.5^\circ\text{C.}$$

$$(i) \text{ Increase in the entropy of water} = 100 \int_{15+273}^{71.5+273} \frac{d\theta}{\theta}$$

$$= 100 \times 2.3 \log_{10} \frac{344.5}{288}$$

$$(ii) \text{ Decrease in the entropy of steam} = 10 \int_{71.5+273}^{100+273} \frac{d\theta}{\theta}$$

$$= 10 \times 2.3 \log_{10} \frac{373}{344.5}$$

$$\text{Hence increase of entropy} = 17.76 - 1.81 = 15.95 \text{ units.}$$

12.16. Maxwell's Thermodynamical Equations.—According to the First law of Thermodynamics

$$dH = dU + dW \dots \dots \dots (i)$$

If a substance expands by dv against a pressure p , work done is $dW = p.dv$ and (i) becomes.

$$dH = dU + p.dv, \dots \dots \dots (ii)$$

Also from the relation for entropy

$$d\phi = \frac{dH}{T}, \text{ (putting } T \text{ for } \theta),$$

we get

$$dH = Td\phi. \quad \dots \quad \dots \quad \dots \quad (iii)$$

Substituting (iii) in (ii),

$$Td\phi = dU + p dv. \quad \dots \quad \dots \quad \dots \quad (iv)$$

Now if ϕ , U , v be considered functions of x and y ,

$$\left. \begin{aligned} d\phi &= \frac{\partial \phi}{\partial x} dx + \frac{\partial \phi}{\partial y} dy. \\ dU &= \frac{\partial U}{\partial x} dx + \frac{\partial U}{\partial y} dy, \\ dv &= \frac{\partial v}{\partial x} dx + \frac{\partial v}{\partial y} dy. \end{aligned} \right\} \quad \dots \quad \dots \quad (v)$$

and

Substituting (v) in (iv) we have,

$$T \left(\frac{\partial \phi}{\partial x} dx + \frac{\partial \phi}{\partial y} dy \right) = \left(\frac{\partial U}{\partial x} dx + \frac{\partial U}{\partial y} dy \right) + p \left(\frac{\partial v}{\partial x} dx + \frac{\partial v}{\partial y} dy \right) \quad (vi)$$

Equating the coefficients of dx and of dy on both sides of (vi),

$$\frac{T\partial\phi}{\partial x} = \frac{\partial U}{\partial x} + p \frac{\partial v}{\partial x} \text{ and } \frac{T\partial\phi}{\partial y} = \frac{\partial U}{\partial y} + p \frac{\partial v}{\partial y}$$

$$\text{or } \frac{\partial U}{\partial x} = \frac{T\partial\phi}{\partial x} - p \frac{\partial v}{\partial x} \text{ and } \frac{\partial U}{\partial y} = \frac{T\partial\phi}{\partial y} - p \frac{\partial v}{\partial y}. \quad \dots \quad (vii)$$

$$\text{Now } \frac{\partial}{\partial y} \left(\frac{\partial U}{\partial x} \right) = \frac{\partial}{\partial x} \left(\frac{\partial U}{\partial y} \right)$$

$$\therefore \frac{\partial}{\partial y} \left(T \frac{\partial \phi}{\partial x} - p \frac{\partial v}{\partial x} \right) = \frac{\partial}{\partial x} \left(T \frac{\partial \phi}{\partial y} - p \frac{\partial v}{\partial y} \right)$$

After simplification, we get

$$\frac{\partial T}{\partial x} \cdot \frac{\partial \phi}{\partial y} - \frac{\partial T}{\partial y} \cdot \frac{\partial \phi}{\partial x} = \frac{\partial p}{\partial x} \cdot \frac{\partial v}{\partial y} - \frac{\partial p}{\partial y} \cdot \frac{\partial v}{\partial x} \quad \dots \quad (viii)$$

Now x and y can be any two variables out of p , v , T , ϕ .

First Equation of Maxwell. Put $x=v$ and $y=T$ in (viii)

$$\begin{aligned} \left(\frac{\partial T}{\partial v} \right)_T \cdot \left(\frac{\partial \phi}{\partial T} \right)_v - \left(\frac{\partial T}{\partial T} \right)_v \cdot \left(\frac{\partial \phi}{\partial v} \right)_T \\ = \left(\frac{\partial p}{\partial v} \right)_T \cdot \left(\frac{\partial U}{\partial T} \right)_v - \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial U}{\partial v} \right)_T \end{aligned} \quad (ix)$$

where, for instance, $\left(\frac{\partial \phi}{\partial T} \right)_v$ means change in entropy, ϕ , with a change in temperature T , when volume, v , of the substance is kept constant and similarly for others. Now $\left(\frac{\partial T}{\partial v} \right)_T$ when T is constant, is

zero, so also $\left(\frac{\partial v}{\partial T} \right)_v$ is zero, and $\left(\frac{\partial T}{\partial T} \right)_v$ and $\left(\frac{\partial v}{\partial v} \right)_T$ are both unity.

Hence (ix) reduces to

$$\left(\frac{\partial \varphi}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \quad \dots \quad \dots \quad \text{I}$$

Clapeyron's Equation can be easily obtained from relation I of Maxwell.

Multiplying both sides of I by T,

$$T\left(\frac{\partial \varphi}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v$$

Since T is constant, T on the left side can be taken within the brackets, and

$$\left(\frac{T \partial \varphi}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v$$

or

$$\left(\frac{dH}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v$$

For a liquid, $dH=L$, the latent heat (Art. 12.9) and $dv=v_2-v_1$, the change of volume,

$$\begin{aligned} \text{Hence,} \quad \frac{L}{v_2-v_1} &= T\left(\frac{\partial p}{\partial T}\right)_v \\ \therefore \frac{dp}{dT} &= \frac{L}{T(v_2-v_1)} \end{aligned}$$

Second Equation of Maxwell. Putting $x=p$, and $y=T$ in (viii)

$$\left(\frac{\partial T}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_p - \left(\frac{\partial T}{\partial T}\right)_p \left(\frac{\partial \varphi}{\partial p}\right)_T = \left(\frac{\partial p}{\partial p}\right)_T \left(\frac{\partial v}{\partial T}\right)_p - \left(\frac{\partial p}{\partial T}\right)_p \left(\frac{\partial v}{\partial v}\right)_T.$$

This simplifies to

$$\left(\frac{\partial \varphi}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \quad \dots \quad \dots \quad \dots \quad \text{II}$$

Multiplying both sides by T

$$\left(T \frac{\partial \varphi}{\partial p}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_p \quad \dots \quad \dots \quad \dots \quad (x)$$

Now $\alpha = \frac{1}{v} \cdot \frac{\partial v}{\partial T}$ is the coefficient of volume expansion under constant pressure

\therefore (x) reduces to

$$\left(\frac{\partial H}{\partial p}\right)_T = -T.v.\alpha.$$

For the **III relation** put $x=\varphi$ and $y=v$ and for the **IV relation** put $x=\varphi$ and $y=p$ in (viii). We get easily

$$\left(\frac{\partial T}{\partial v}\right)_\varphi = \left(\frac{\partial p}{\partial \varphi}\right)_v \quad \dots \quad \dots \quad \dots \quad \text{III}$$

and

$$\left(\frac{\partial T}{\partial p}\right)_\varphi = \left(\frac{\partial v}{\partial \varphi}\right)_p \quad \dots \quad \dots \quad \dots \quad \text{IV}$$

QUESTIONS

1. Carefully distinguish between reversible and irreversible operations and state the conditions for reversibility. Is it possible to realise reversibility in actual practice?

2. Write a brief note on the second law of thermodynamics and show that the Kelvin and Clausius forms are two ways of looking at the same problem.

3. Discuss the working of a Carnot engine. Bring out its importance. Show that its efficiency is maximum but its power is zero.

4. Justify "All reversible engines working between the same temperature limits have the same efficiency."

5. Distinguish between the ideal gas scale, the platinum resistance scale and the work scale of temperature. State the merits and demerits of each system.

6. Briefly explain the Kelvin's scale of temperature. Establish the identity between it and the ideal gas scale.

7. What is entropy? State its importance and show that the entropy of the universe tends to a maximum.

8. How is it possible to define temperature in terms of energy and arrive at absolute scale from thermodynamic considerations?

9. Determine the rate of change of saturation pressure with temperature for water at 100°C , given: latent heat of water at $100^{\circ}\text{C} = 539 \text{ cal.}$
 $J = 4.2 \times 10^7 \text{ ergs/cal.}$, volume of steam formed 1670 c.c.

[Hint:—

$$\begin{aligned} dp/d\theta &= \frac{539 \times 4.2 \times 10^7}{373(1670-1)} \times \frac{76}{1.013 \times 10^6} \text{ cm. of Hg/}^{\circ}\text{C.} \\ &= 2.7 \text{ cm. of mercury/}^{\circ}\text{C at } 100^{\circ}\text{C}. \end{aligned}$$

10. 30 grams of water at 50°C are mixed with 50 grams of water at 30°C . Calculate the change of entropy.

11. If there is no wastage of energy in the carnot reversible engine, why is its efficiency less than unity?

12. Deduce an expression for the efficiency of a carnot engine or show that the efficiency of a carnot engine is

$$E = 1 - \frac{T_2}{T_1}$$

13. Deduce the Clapeyron's equation (i) by considering a carnot cycle (ii) from Maxwell's First equation.

14. Write an essay on Entropy and bring out the importance of entropy in thermodynamics.

15. Show that the change of entropy in a reversible cycle is zero but that in all actual processes, Entropy tends to a maximum.

16. Explain the statement, "The Entropy of a substance is a measure of the degree of disorder prevailing among its molecules."

17. Deduce an expression for the entropy of an ideal gas.

Calculate the Change of entropy in 4 gm. of hydrogen when its volume is halved and the temperature changed from 0°C to 100°C .

18. Deduce the Maxwell's Equations.

$$(i) \quad \left(\frac{\partial \phi}{\partial v} \right)_T = \left(\frac{\partial p}{\partial T} \right)_v$$

$$(ii) \quad \left(\frac{\partial \phi}{\partial p} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_p$$

CHAPTER XIII

CONDUCTION

The man who never made mistakes, never made anything. Make your mistakes the stepping-stones to success. When you do anything do it so well that there is no need to do it again.—*Nehru*.

I shall abide by my reason, because with all its weakness there is some chance of getting at truth with it.

—*Vivekanand*.

13.1. Heat can travel in three ways—by Convection, by Conduction and by Radiation.

In the process of **Convection**, heat spreads in a body by *the actual movement of its molecules* and by its very nature is possible only in liquids and gases. The molecules near the source of heat, absorb some of the heat, expand and get lighter, and therefore rise up giving their places to their colder neighbours which also behave likewise. Convection currents are thus produced in the liquid and gradually the whole mass is heated up.

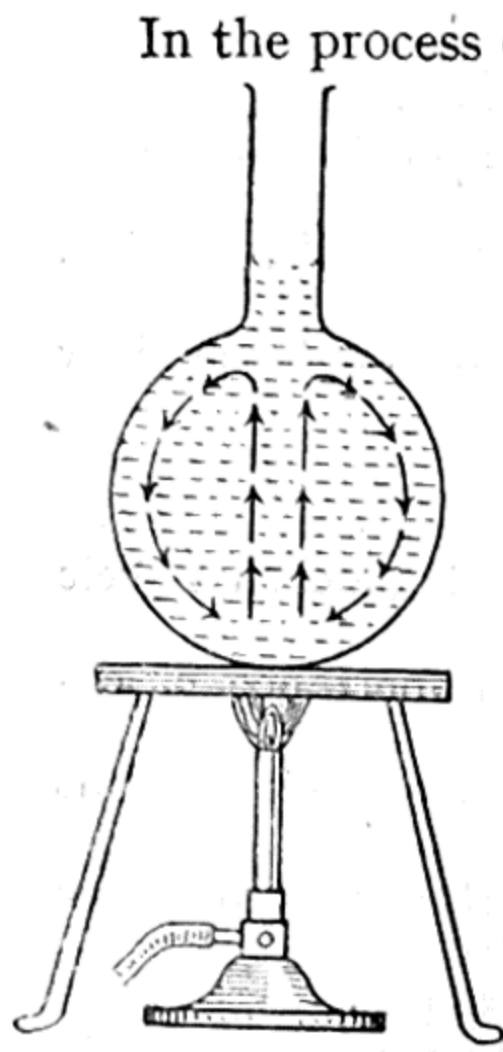


Fig. 13.1
Convection of heat.

In the process of **Conduction**, heat flows from the hotter parts of a body towards its colder parts *without any visible movements of the molecules taking place*. The molecules at the hot end absorb energy from the source of heat. This increase of heat increases the molecular kinetic energy. The molecules begin to vibrate *about their mean positions* faster than before. They transfer a part of their energy by collisions to their slower-moving neighbours, with the result that the latter quicken their vibrations (and hence show a rise of temperature). The absorption of heat from the source and its transference from one layer of molecules to the next, by collisions, continues till the heat reaches the most distant parts of the body. We find that in *conduction the molecules keep on oscillating about their mean positions while heat travels onwards*. Conduction is a very slow process because heat has to travel from molecule to molecule.

Conduction of heat is possible only if differences of temperature exist between the various parts of a body and the flow of heat always occurs in the direction of fall of temperature. Heat travels by conduction in solids, but may travel in liquids and gases as well by the same process under suitable conditions.

In the process of **Radiation**, heat travels *directly* from one body to another, the intervening medium exhibiting no rise of temperature. The rapidly oscillating molecules of the hot body produce waves in the all-pervading *ether*. The waves carry the energy, which they have absorbed from the hot body with them, and when they fall on the surface of a colder body they transfer their energy to its molecules. The molecular kinetic energy of the latter increases and a rise of temperature manifests itself. The heat thus transferred is called **Radiant Heat** to denote its method of transmission. It travels in straight lines and shares the other properties of the light waves. Heat comes to us from the Sun in this way,

A metal rod with one end in fire is heated by *conduction*, a kettle of water placed over the fire is heated by *convection* while a person sitting in front of the fire gets the heat by *radiation*.

13.2. Conduction along a Metal Rod.—If one end of a metal rod be projected into a steam chamber and thermometers be placed in holes drilled into it at equal distances along its length, it is observed that the thermometer nearest the hot end is first affected, but gradually the heat travels onwards and one thermometer after the other begins to show a rise of temperature. Since the temperature at various points of the rod is changing, its state is said to be *variable*. A portion of the total heat that enters any section of the rod is retained by it to raise its own temperature, another portion of the heat is transmitted forwards and heats up the next section while the rest of the heat is lost by radiation from the surface of the rod. The more distant a section is from the hot end, the greater is the proportion of heat which is lost by radiation from the portion of the rod between the hot end and the particular section and therefore, the lower is its temperature. If the loss of heat by radiation be diminished by covering the rod with felt, the various portions of the rod will show higher temperatures than before. In the *initial* stages of heating, the specific heat of the material also plays an important part. If the specific heat is low, the rod will show a higher temperature for a given amount of heat absorbed, than otherwise.

For some time, the temperature at various points goes on rising till the steady state is reached. Thereafter, the temperatures indicated by the various thermometers become constant and cease to rise any further. This shows that no more heat is being retained by any section of the rod. After the steady state has been attained, the specific heat ceases to play any part whatsoever, because no portion of the heat is being retained to produce a rise of temperature.

13.3. Thermal Conductivity.—The quantity of heat flowing across a parallelopiped after the stationary state has been reached depends

(1) on the area, A , of the face H , on which the heat is incident; the larger this area is, the larger is the flow of heat,

(2) on the difference of temperature, $(\theta_1 - \theta_2)$, between the hot face

H and the cold face C ; the greater this difference of temperature is, the more rapid will be the flow of heat,

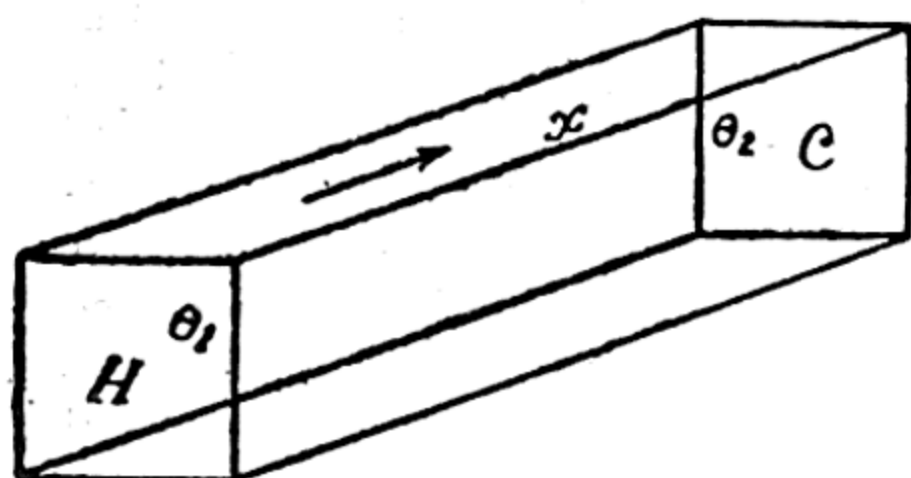


Fig.13.2.

Flow of heat across a rod.

Since the heat flows from molecule to molecule, it will flow faster if a smaller depth of the molecules has to be crossed.

Combining all the above factors

$$Q = -K.A. \frac{\theta_1 - \theta_2}{d} . t$$

the negative sign is put because the temperature decreases as the distance from the hot end increases.

K is called the **Thermal conductivity** of the material. *It is the amount of heat that flows per second across one centimeter of the material having one square centimeter face-area, when a unit temperature difference exists between its hot and cold faces.*

If only small sections of the material are considered at a time (and not the whole rod together), we have

$$Q = -K.A. \frac{d\theta}{dx} . t$$

$\frac{d\theta}{dx}$ is called the *temperature gradient* and is the tangent of slope of a curve showing temperature against distance, at a point distant x from the hot end.

Example.—The thickness of ice on a lake is 10 cm. and the temperature of air is -10°C . At what rate is the thickness of ice increasing at this moment and approximately how long will it take for the thickness to be doubled? [Thermal conductivity of ice $= 0.004 \text{ cal cm.}^{-1} \text{ sec}^{-1} \text{ }^\circ\text{C}^{-1}$, density of ice $= 0.92 \text{ gm/cc}$. Latent heat of ice 80 cal/gm .]

$$Q = -\frac{K.A. (\theta_1 - \theta_2) t}{d}$$

$$K = 0.004 ; \theta_1 - \theta_2 = [0 - (-10)] = 10 ; t = 1 ; d = 10$$

$$Q = \frac{0.004 \times A \times 10 \times 1}{10} = 0.004 A \text{ calories.}$$

$$\text{Ice formed} = \frac{0.004 A}{80} \text{ gm.}$$

$$= \frac{0.004 A}{80 \times 0.92} \text{ c.c.}$$

$$\therefore \text{Rate of increase of thickness of ice} = \frac{0.004 A}{80 \times 0.92 \times A} \text{ cm./sec.}$$

$$= 54 \times 10^{-6} \text{ cm./sec} \quad \dots(i)$$

Time reqd. for thickness to be doubled

$$\text{i.e., to be increased by 10 cm.} = \frac{10}{54 \times 10^{-6}} \text{ sec.}$$

$$= 1.85 \times 10^5 \text{ sec.} \quad \dots(ii)$$

13.4. Flow of heat in a bar of Uniform Cross-section.

Consider a rod of uniform cross-section which is being heated

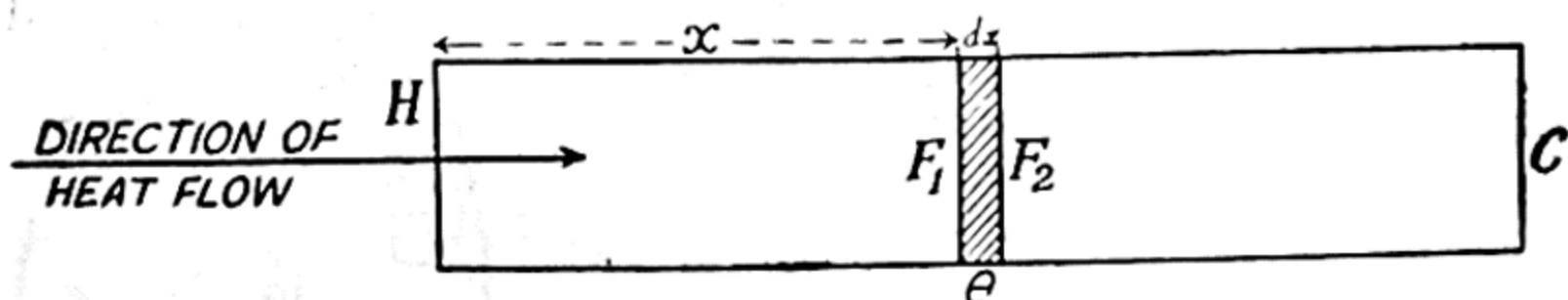


Fig. 13.3. Flow of heat along a rod.

at the end H . Heat is flowing in the direction of the arrow towards the cold end C . Consider a vertical section of the rod of thickness dx at a distance x from the hot end and let the temperature at the face F_1 of this section be θ . The temperature-gradient at the face F_1 is $d\theta/dx$ and the heat flowing through it per second is $-K.A. d\theta/dx$.

The temperature at the face F_2 is $\theta + \frac{d\theta}{dx} \cdot dx$ and the temperature-gradient there is $\frac{d}{dx} \left(\theta + \frac{d\theta}{dx} \cdot dx \right)$. The heat following out through F_2 per second is

$$-KA \frac{d}{dx} \left(\theta + \frac{d\theta}{dx} \cdot dx \right)$$

The net gain of heat by the section dx is

$$-KA \frac{d\theta}{dx} - \left[-KA \frac{d}{dx} \left(\theta + \frac{d\theta}{dx} dx \right) \right]$$

$$= KA \frac{d^2\theta}{dx^2} \cdot dx$$

This heat is being partly used up in raising the temperature of the section and is being partly lost by radiation from its surface. If ρ be the density of the material of the rod, the weight of the section is

$A \cdot dx \cdot \rho$ and if $\frac{d\theta}{dt}$ be the rate of rise of temperature and S the specific

heat of the material, the heat retained by the section for a rise of its

temperature is $A dx \cdot \rho \cdot S \cdot \frac{d\theta}{dt}$. The loss of heat by radiation is pro-

portional to the area of the surface of the section i.e., to $p \cdot dx$ where p is the perimeter of the section, to the excess of temperature θ of the

rod over surroundings and to its emissive power E , and is equal to $E \cdot p \cdot dx \cdot \theta$. Hence

$$(i) \dots KA \frac{d^2\theta}{dx^2} \cdot dx = \rho \cdot A \cdot dx \cdot S \frac{d\theta}{dt} + E \cdot p \cdot dx \cdot \theta.$$

when the steady state is reached, the first term on the right vanishes

$$\text{and } (ii) \dots KA \frac{d^2\theta}{dx^2} \cdot dx = E \cdot p \cdot \theta \cdot dx.$$

$$\text{or } \frac{d^2\theta}{dx^2} = \frac{Ep}{kA} \cdot \theta = m^2\theta. \dots (i)$$

To solve this equation put $\theta = e^{nx}$.

$$\frac{d\theta}{dx} = n \cdot e^{nx}$$

$$\text{and } \frac{d^2\theta}{dx^2} = n^2 \cdot e^{nx}.$$

Substituting in (i) $n^2 = m^2$ or $n = \pm m$
and $\theta = e^{mx}$ or, e^{-mx}

The general solution is

$$\theta = A e^{mx} + B e^{-mx}$$

where A and B are constants depending upon the conditions prevailing.

13.5. Measurement of Conductivity. In the Searle's method, one end of the experimental rod is projected into a steam chamber, while the other projects into a chamber filled with ice. Two thermo-

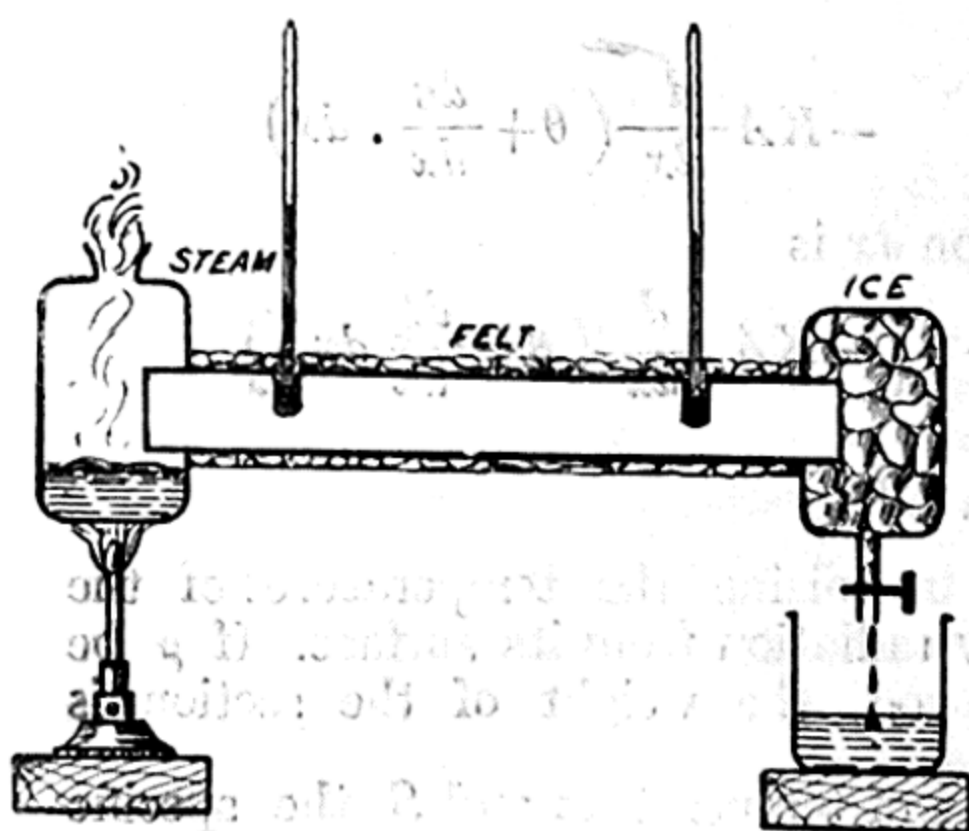


Fig. 13.4

eti lo Searle's method for K .

meters are inserted into holes drilled one near each end and the rod is carefully packed with felt to prevent loss of heat by radiation from its surface. The temperatures of the two thermometers are noted after the steady state has been reached. The heat flowing in a given time across the rod is calculated from the weight of ice melted. The distance between the two thermometers and the area of cross-section of the rod are also measured. K is determined by using the relation

$$Q = -KA \frac{\theta_1 - \theta_2}{d} \cdot t$$

The method, though straightforward, is not capable of great

accuracy because loss of heat by radiation cannot be entirely eliminated, no perfect insulator of heat being known.

13.6. Forbe's Method for K. In the method due to Forbe the rod is not padded. Radiation occurs freely and the total heat thus lost by the rod can be calculated. Two experiments have to be performed the *statical* and the *dynamical*.

(1) **Statical Experiment.** One end of a rectangular metal rod, 7 feet long and $1.25'' \times 1.25''$ cross-section, is inserted in a cast-iron cup C containing molten lead. The molten lead is maintained at a constant temperature by adding fresh pieces of lead to it from time to

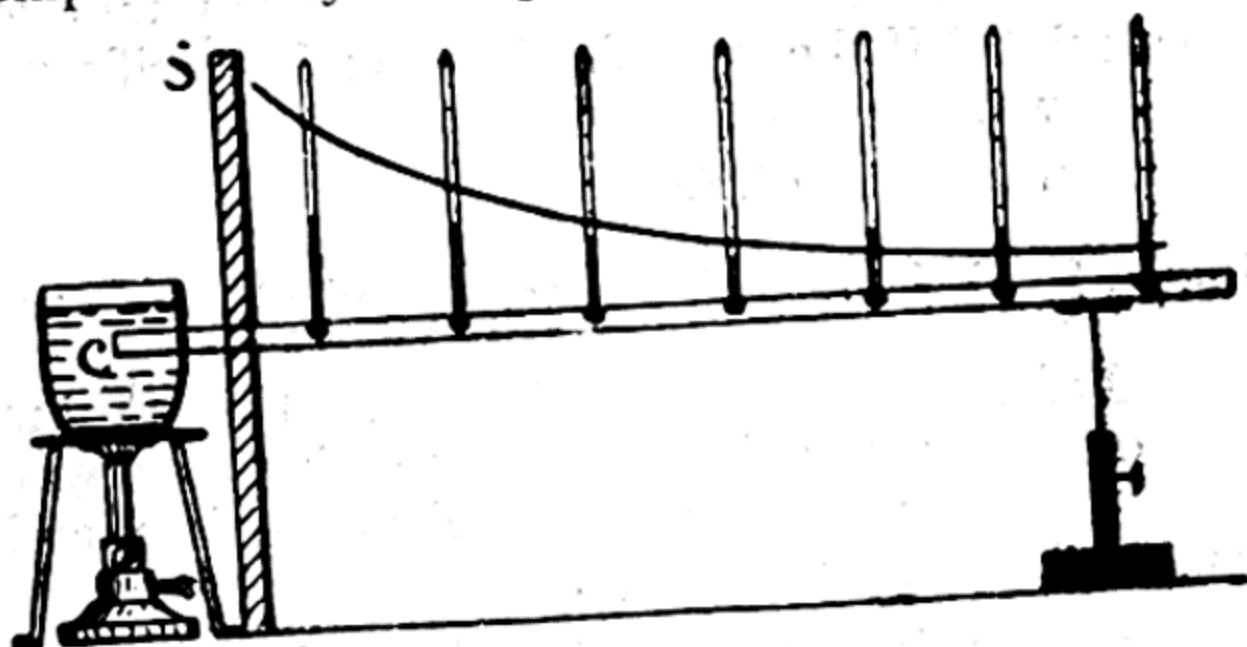
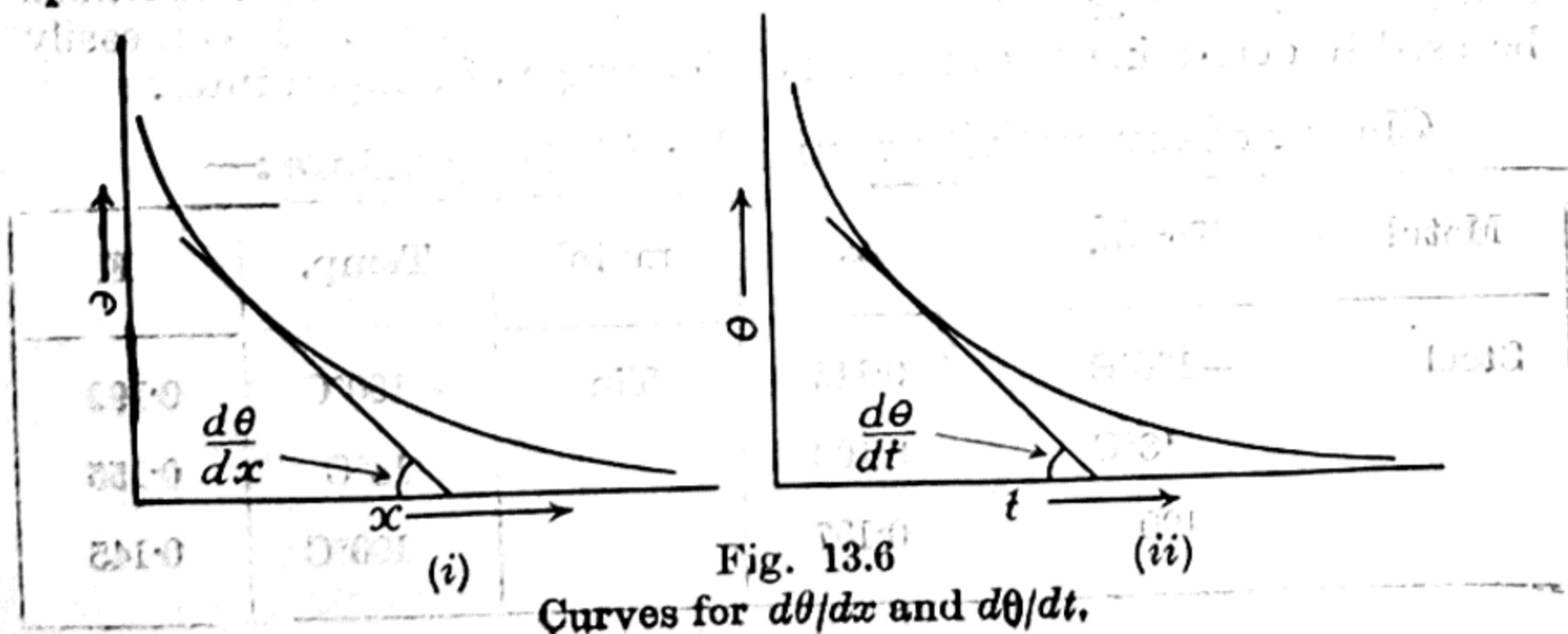


Fig. 13.5
Forbes' method for K.

time. The rod is painted white and thermometers are placed, all along its length at 3'' intervals into holes bored in the rod. A wooden screen S, protects the thermometers from gaining heat directly from the bath by radiation. When after about 8 hours, the steady state has been reached, the various thermometers are read. The thermometers at the distant end are hardly affected and only indicate the room temperature. A curve is then plotted between the temperature θ at any point and the distance x of the point from the hot end.

The slope of the tangent to this curve at any point gives $\frac{d\theta}{dx}$ there.

This is called the *statical experiment* because the temperature at every point of the rod becomes stationary before observations are recorded.



(2) **Dynamical Experiment.** A rod identical with the previous one in cross-sectional area and in the nature of its surface but only 21" long is heated to the temperature of the molten lead. It is then placed on two poorly conducting knife-edges and allowed to cool. Its temperature is recorded every half-minute by means of a thermometer placed in a hole drilled in the middle of the rod. A curve showing *excess* of temperature of the rod over its surroundings against time is plotted. The slope $\frac{d\theta}{dt}$ of this curve at any point gives the rate at which *temperature* falls for that particular excess of temperature. The heat lost per second for that temperature-excess by unit length of the rod can be calculated if the specific heat and specific gravity of the material are known.

Heat lost per second, $M.S.\theta$

$$= (\text{volume of unit length of rod} \times \text{sp. gravity}) \times \text{specific heat} \times \frac{d\theta}{dt}.$$

$d\theta/dt$ is the fall of temperature in unit time. This also measures the heat, Q , that crosses any section of the rod, in the steady state. K is determined by dividing Q by the area A of the face and by the fall of temperature $d\theta/dt$ per unit length.

Proceeding in this manner, the thermal conductivity of the material can be determined for various temperatures. K is found to depend on temperature.

The method is open to the following objections :—

(1) The molten bath can never be kept at one uniform temperature for hours together.

(2) The steady state is never truly reached in such a big rod.

(3) Newton's law of cooling is supposed to be true for various temperature-excesses, for which there appears to be no justification.

(4) The method is very round-about, long specimens of the material have to be used and prolonged heating is necessary.

(5) It cannot be directly used for studying the variations of K with temperature with any great accuracy.

The following method due to Lee is free from these objections and is a much neater and a very compact arrangement. It can easily be used to determine K over a very wide range of temperatures.

Change of conductivity of metals with temperature :—

Metal	Temp.	K.	metal	Temp.	K
Steel	−160°C	0.113	Tin	−160°C	0.192
	18°C	0.108		18°C	0.155
	100	0.107		100°C	0.145

13.7 Lee's method for Metals (conductors). A small rod L of the metal 7 cm. long and .58 cm. section is held in a socket provided in a thick copper disc D , which is itself secured to the lower end of a copper cylinder C . This cylinder is supported in a Dewar flask in which any desired temperature can be produced and *maintained* (because escape of heat is difficult across the flask). Two brass sleeves T_1 and T_2 are placed round L and can easily be adjusted at any desired distance from each other. Platinum wires of two resistance thermometers are wrapped round T_1 and T_2 and a heating coil H is provided at the top of the rod. By varying the current through H , any suitable temperature-difference can be established between the points T_1 and T_2 on the rod.

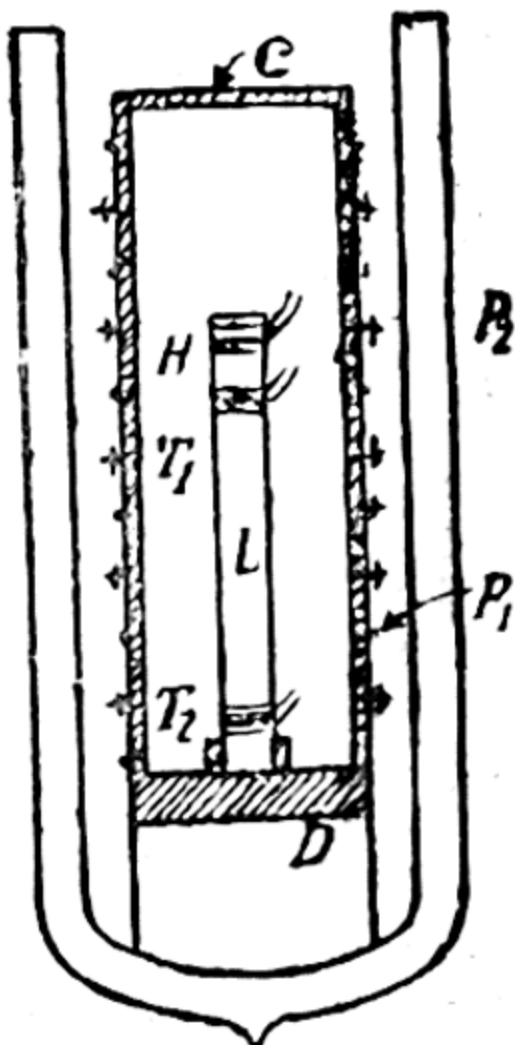


Fig. 13.7
Lee's method for metals

In order to determine the conductivity of the substance at any temperature, it is first cooled a few degrees below that temperature (if it is not already at a lower temperature) by pouring liquid air into the flask. When the necessary cooling has been produced, the remaining liquid air is poured off. The evaporation of the liquid air leaves the apparatus *dry* and this is the merit of using liquid air as a cooling agent. The rod is now warmed up to the desired temperature by passing an electric current through the coil P_2 which is wrapped round the copper cylinder C . When the desired temperature has been reached, this current is now switched off. A current is then sent through H , the strength I of the current is measured with a sensitive ammeter joined in series with H and the P.D., E , between its ends is indicated by an accurate voltmeter joined in parallels across them. When the steady state has been reached, the temperatures θ_1 and θ_2 indicated respectively by T_1 and T_2 are noted. Conductivity is calculated by equating

the heat $\frac{EIt}{4.2}$ calories generated by the current to the heat

$K.A. \frac{\theta_1 - \theta_2}{d} . t$ flowing across the rod. Hence

$$KA. \frac{\theta_1 - \theta_2}{d} . t = \frac{E.I.t}{4.2}$$

$$K = \frac{E.I.d.}{4.2A(\theta_1 - \theta_2)} \quad \dots (i)$$

There is, however, an important source of error in this experiment. The heat from the rod flows into the copper cylinder which is warmed up as a consequence and then tends to raise the temperature of the rod itself by radiating heat to it. This means, in other words,

that the steady state is never truly reached. The consequence of this heat radiation is that the temperature of the thermometer T_2 is higher than it would have been otherwise. To estimate the error due to this cause, a coil of wire P_1 having exactly the same resistance as H is wrapped round the cylinder C and a current is sent round it for some time till T_1 and T_2 indicate steady temperatures. This is done before starting the main experiment and also after the main experiment is over. If d_1 and d_2 are the temperature-differences between T_1 and T_2 (T_2 indicating the higher temperature) in the two cases, the correct

difference of temperature between T_1 and T_2 will be $(\theta_1 - \theta_2) + \left(\frac{d_1 + d_2}{2}\right)$

and not $(\theta_1 - \theta_2)$ as given in equation (i). This correction is accordingly made.

Since only small samples of metals are needed and since the apparatus can be built up in a Dewar flask, it is an ideal arrangement for determining K at different temperatures.

13.8 Angstrom's method for K . In this arrangement, one end of the experimental rod is alternately heated and cooled. The end projects into a chamber through which steam at a known temperature is passed for 12 minutes. Steam is now shut off and cold water at a known temperature is then circulated for 12 minutes. The water is now replaced by steam again, and so on. Whenever the end is heated a heat-wave travels outwards from it and when it is cooled a heat-wave flows towards it and these two waves flow alternately across the rod in opposite directions. When heating has continued long enough, the periods develop themselves completely, in which case the mean temperature at any point of the bar preserves some constant value. Moving the junction of a thermocouple along the rod, a point such as A is determined showing the maximum temperature. Taking another couple and moving it towards the right a point B similar to A is found. Then $AB = \lambda$, the wavelength of the temperature wave. The time $t = 24$ minutes,

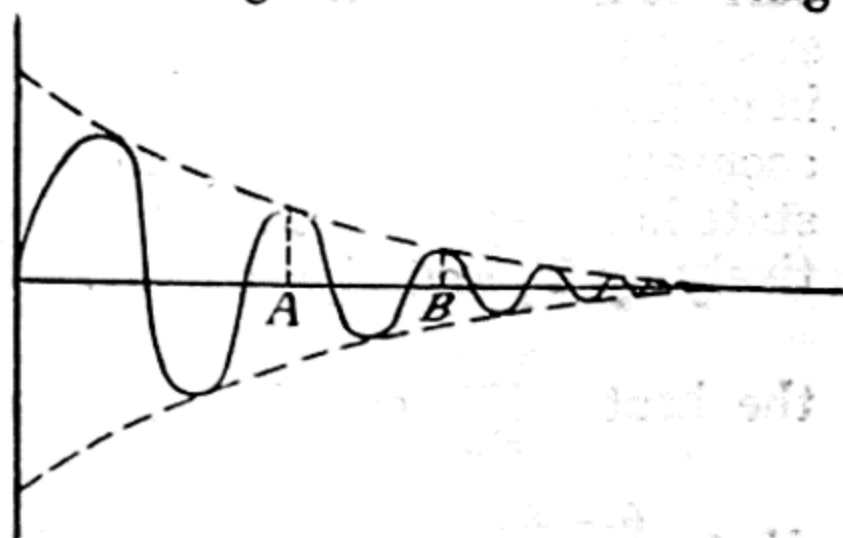


Fig. 13.8
Angstrom's method for K .

Conductivity is determined by using the relation

$$\frac{K}{\rho S} = \frac{\lambda^2}{4\pi t}$$

where ρ is the sp. gravity and S the sp. heat of the material of the rod.

Thermal conductivities of metals at ordinary temperatures.

Metal	K
Aluminium	0.504
Copper	0.918
Steel	0.113
Lead	0.083
Mercury	0.0197
Silver	0.974
Brass	0.260

13.9. Conductivity and Age of the Earth. The above method has been used to determine the conductivity of the earth's crust. The earth is heated up during day-time and cools down during the night and a *daily* heat-wave penetrates into the earth's crust. Again, there is also an *annual* wave because the earth absorbs more heat during summer than during winter. The temperatures at various depths are measured by embedding thermometers and K is determined by using the above formula (art. 13.8). The daily wave reaches a depth of about 3 feet, but it is found that the annual wave penetrates about 19 times as much as the daily wave does. Its progress into the earth is, however, very slow, *i.e.*, 4 cm. per day only.

The temperature rises steadily at the rate of 1°F per every 60 feet of descent into the earth's interior. Hence heat must be flowing all the time from the interior of the earth outwards. Lord Kelvin has tried to calculate the age of the earth from a knowledge of the rate of loss of heat from its surface. Kelvin thinks that when the earth was in a molten condition, the temperature throughout the fluid mass was 3900°C . The problem is how long will it take for the earth to cool from 3900°C , for the present temperature gradient to be attained, supposing that the surface temperature of the earth now is approximately 0°C . He finds that at the present rate of loss of heat by the earth it must be over 100 million years when the earth was in a molten condition. This estimate is however too short, because the radio-active bodies inside the earth are continually generating large amounts of heat by spontaneous dis-integration. This will continually slow down the cooling of the earth.

By a study of the proportions of isotopes of lead in radio-active rocks, Professor Holmes of Edinburgh (1946) has put the period at 3,350 million years. This has been done in two ways.

(i) By losing successively 8 α -particles, the radio-active uranium is converted into stable *RaG* (which is lead). Knowing the proportion of lead in Uranium-bearing rocks, and the rate of dis-integration of Uranium, the age of the oldest rocks on the earth can be calculated.

(ii) The α -particles lost by the Uranium are retained by the rocks and are gradually converted into Helium gas which does not escape until the powdered mineral sample is dissolved, fused or heated. The liberated gas can be collected and measured. Knowing the rate of decay of Uranium the age of the rock is determined.

13.10. Conductivity of Crystals.

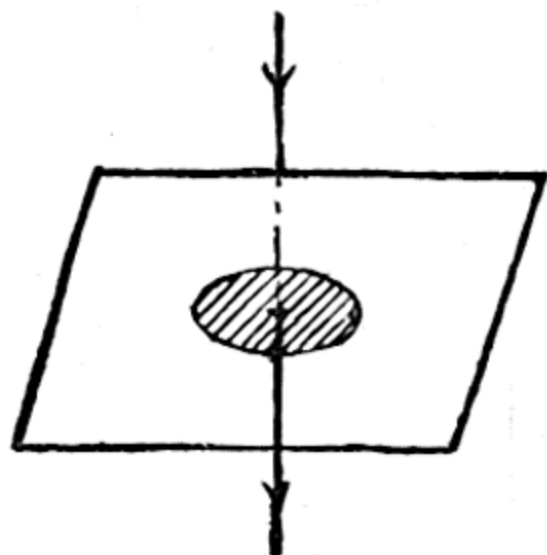


Fig. 13.9
Conductivity of
Crystals.

Although metals have the same conductivity in all directions across them, it is not so in crystals. Their conductivity is usually different along the various axes. This can easily be shown as follows. A thin plate cut out of a crystal is thinly coated with wax and set up horizontally. A resistance wire passes vertically through a hole bored in the centre of the plate. When the wire is heated electrically, the heat flows outwards from the wire on the crystal plate. It is found that the area over which the wax is melted is oval or elliptical in shape. Had the conductivity been the same in all directions, the area would have

been circular.

The actual conductivity along any axis can be determined by cutting a thin plate out of the crystal in a direction perpendicular to the axis and placing it between two metal discs. The top disc is heated and heat flows down the crystalline plate into the lower disc. When the steady state has been reached, conductivity can be calculated in the usual manner.

There is an extra-ordinary increase in the thermal conductivity of crystals at low temperatures. K for a quartz crystal at room temperature is about five times that of quartz glass, but at the temperature of liquid hydrogen it becomes 500 times as much. This has been explained by Eucken on the hypothesis that crystals consist of atomic lattices.

13.11. K for Poor Conductors. The heat flowing across poor conductors like card board, wood, etc. for reasonable differences of temperature between the end faces, will be too small to be measured with accuracy, while the major part of the heat will be lost from their surfaces. In a method due to Lee a circular disc S of the material, 4 cm. in diameter and a mm. or two thick, is held between two similar copper discs C_1 and C_2 . Glycerine is thinly applied to the two faces of S to secure good thermal contacts with C_1 and C_2 . An insulated, flat heating coil of platinum H is placed between C_2 and another copper disc C_3 . The heat produced in the coil quickly spreads over the copper discs and falling on the entire face of S flows normally across it. Since the heat lost by a body depends on the nature of its exposed surface, the pile

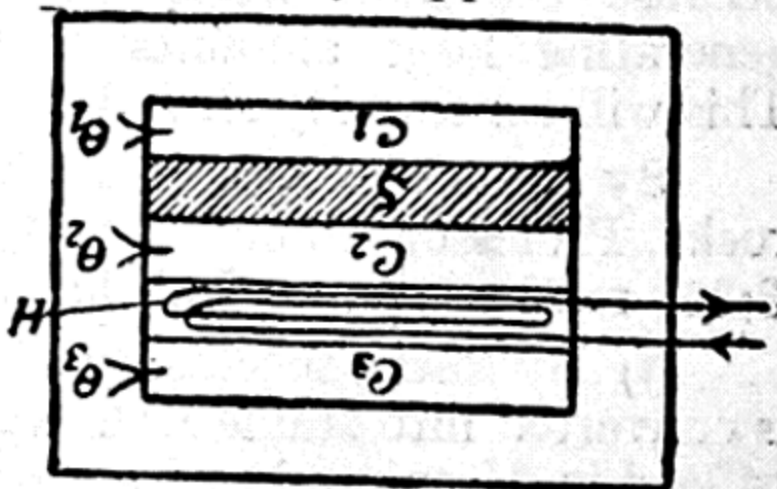


Fig. 13.10

Lee's method for Poor Conductors.

of the discs is varnished over. Thermo-couples are inserted in the disc C_3 on either side of S into C_1 and C_2 in small holes drilled in them for the purpose and the whole arrangement is suspended in a constant temperature enclosure.

The heat flowing across any plane in S in unit time is partly lost by radiation from its own surface while the rest, which is passed on to C_1 is lost from its surface. If a, a_1, a_2, a_3 , be the areas of the exposed surfaces of S, C_1, C_2, C_3 respectively and θ be the temperature of the enclosure, the heat lost from the surface of S is, by Newton's law of cooling, $\sigma \cdot a \cdot \left(\frac{\theta_1 + \theta_2}{2} - \theta \right)$ and the from the surface of C_1 is $\sigma \cdot a_1 (\theta_1 - \theta)$ where σ is a constant depending on the nature of the exposed surface.

The total heat flowing into S is

$$\sigma \cdot a \cdot \left(\frac{\theta_1 + \theta_2}{2} - \theta \right) + \sigma \cdot a_1 (\theta_1 - \theta) \quad \dots(i)$$

and that following out of it is

$$\sigma \cdot a_1 (\theta_1 - \theta). \quad \dots(ii)$$

The heat flowing across any section of S viz., $KA \frac{\theta_2 - \theta_1}{d}$, is the average of the heat flowing into S and the heat flowing out of it.

Hence

$$\begin{aligned} KA \frac{(\theta_2 - \theta_1)}{d} &= \frac{1}{2} \sigma \left[a \left(\frac{\theta_1 + \theta_2}{2} - \theta \right) + a_1 (\theta_1 - \theta) + a_1 (\theta_1 - \theta) \right] \\ &= \frac{\sigma}{2} \left[a \left(\frac{\theta_1 + \theta_2}{2} - \theta \right) + 2a_1 (\theta_1 - \theta) \right] \quad \dots(iii) \end{aligned}$$

To determine σ , we make use of the fact that when the steady state is reached, all the heat that is produced by a current of I amperes at E volts is lost by radiation from the outer surface of the pile of discs ; hence

$$\frac{EI}{4.2} = \sigma [a_3(\theta_3 - \theta) + a_2(\theta_2 - \theta) + a \left(\frac{\theta_1 + \theta_2}{2} - \theta \right) + a_1(\theta_1 - \theta)] \quad \dots(iv)$$

using the value of σ from (iv) in (iii), K can be calculated.

The poor conductors find a ready application in designing the walls of ice-houses, furnaces and boilers. Materials, whose conductivity is the least, are employed, to cut down the flow of heat across the walls to a minimum.

K for poor conductors.

Poor Conductor	Conductivity	Poor Conductor	Conductivity
Window glass	2.5×10^{-3}	Mica	1.8
Teak wood	0.6	Paper	0.3
Asbestos	0.3	Rubber	0.45
Card board	0.5	Sand	0.13
Cotton wool	0.06	Silk	0.22
Cork	0.11	Slate	4.7
Felt	0.09		

13.12. Laboratory Method for K for Poor Conductors.

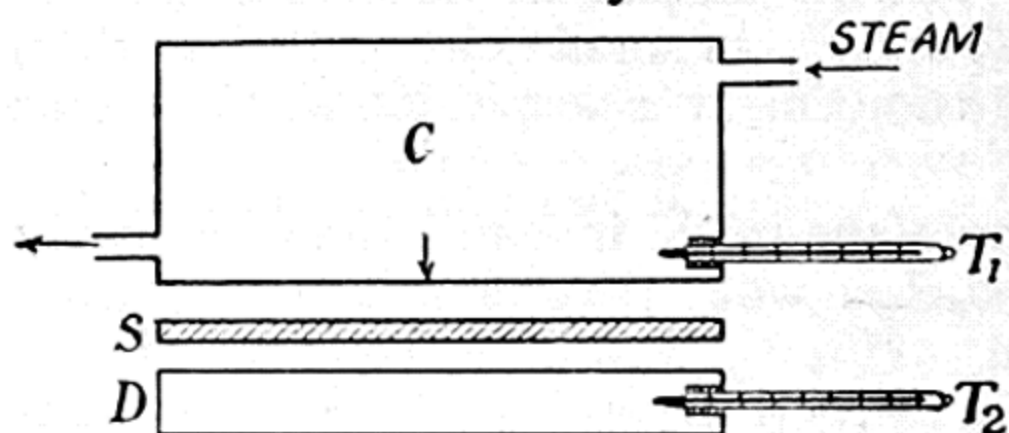


Fig. 13.11.

K for poor conductors.

poorly conducting material is available in the form of a *thin* disc S e.g., rubber, leather, cardboard, it is placed in between a hollow box of copper C through which steam is flowing and a copper disc D . The surfaces of C and D are nickel-plated to obtain good emissivity. The three i.e. C ,

S and D are placed in *close* contact. Heat will flow vertically downwards in the direction of the arrow. The temperatures on either side of S are read on the thermometers T_1 and T_2 embedded in C and D but *close* to S . Let their readings in the steady state be T_1 and T_2 .

If d be the thickness of S and K its thermal conductivity, heat flowing through it per second is

$$K \frac{T_1 - T_2}{d} \cdot A \quad \dots (i)$$

where A is the area of cross-section of S .

To calculate the rate of loss of heat from D (the loss from the curved surface of S is negligible, because its thickness, d , is very small) in order to calculate K , a cooling curve is plotted for D for a temperature-range $(T_2 + 20^\circ)$ to $(T_2 - 20^\circ)$ from which its rate of cooling, $d\theta/dt$, at the temperature T_2 can be obtained. If M be the mass of D and s the sp. heat of its material, the heat lost by it per second is

$$M.s. \frac{d\theta}{dt}.$$

Equating it to (i), we get

$$K \cdot \frac{T_1 - T_2}{d} \cdot A = M.s. \frac{d\theta}{dt}$$

from which K can be calculated.

13.13. K by Cylindrical Tube Method.

Let $A B$ be a cylindrical tube of internal radius r_1 , external radius r_2 and length l . Let heat be travelling from inside to the outside. In the steady state the lines of heat-flow will be radial and symmetrical as shown by arrows.

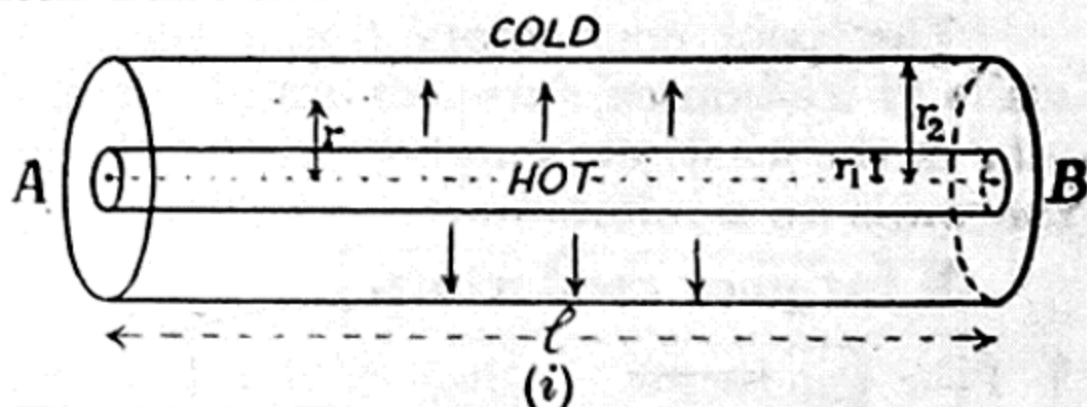


Fig. 13.12. Heat-flow across cylindrical tube shown by arrows. Let θ be the temperature at a distance r from the axis, the temperature gradient is $d\theta/dr$. The heat flowing per second across a shell of radius r is (since area of shell is $2\pi r.l$)

$$Q = -K(2\pi r l) \frac{d\theta}{dr}$$

$$\text{or } Q \cdot \frac{dr}{r} = -K \cdot 2\pi l d\theta$$

Integrating

$$Q \log_e \frac{r_2}{r_1} = -K 2\pi l (\theta_2 - \theta_1)$$

$$\text{and } K = \frac{Q}{2\pi l} \times \frac{\log_e \frac{r_2}{r_1}}{\theta_1 - \theta_2} \dots (i)$$

To determine the thermal conductivity of rubber, a rubber tube (Fig. ii) is taken whose length $l (= AB)$ dips in a calorimeter containing a known mass of water. If θ_1 be the temperature of steam and

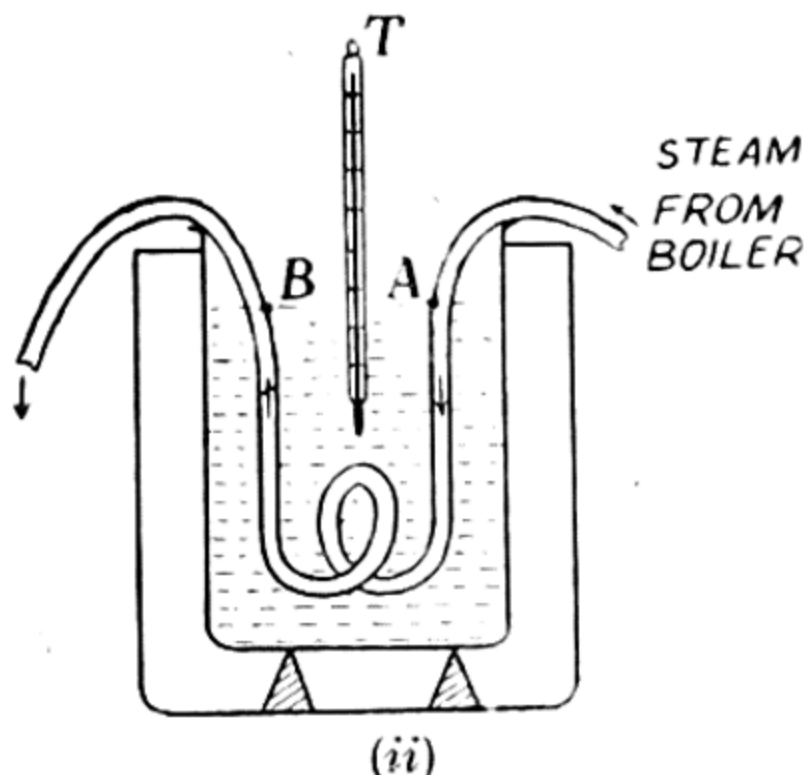


Fig. 13.12. K for rubber tubing

$\theta_2 = \frac{\theta' + \theta''}{2}$ (where θ' and θ'' are the initial and final temperatures of the calorimeter) be the mean temperature of the calorimeter, Q can be easily calculated and K found out using relation (i).

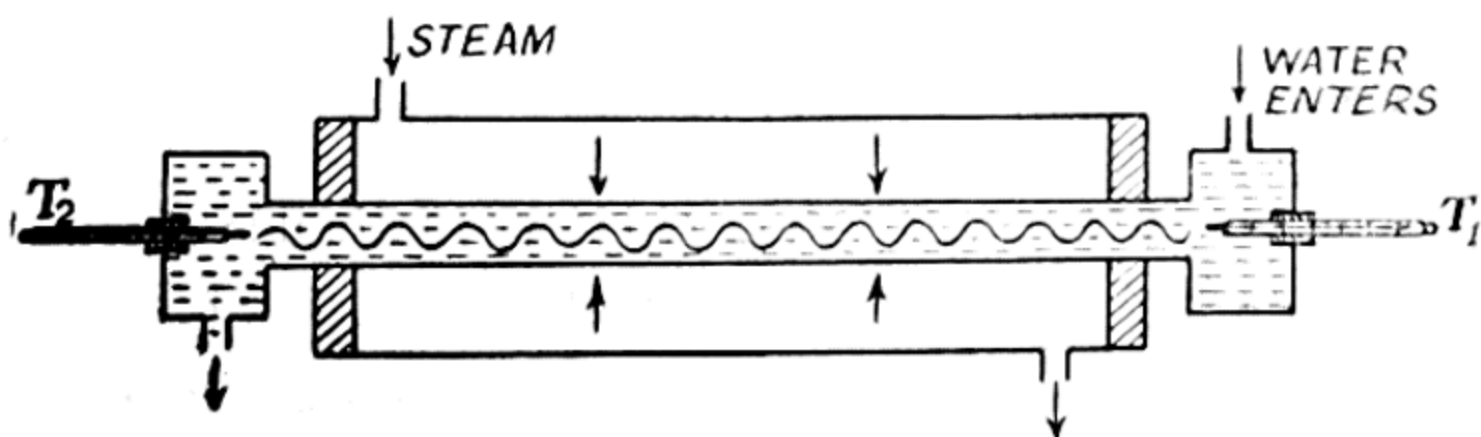


Fig. 13.12. (iii)
K for glass by tube method.

To determine K for glass, given in the form of a tube (Fig. iii), the tube is heated on the outside by surrounding it with a steam jacket, a stream of cold water runs through the tube, the temperature of the water is determined at inlet and outlet. A wire, in zig-zag form is put in the tube to keep the water well-stirred while it is running through the tube.

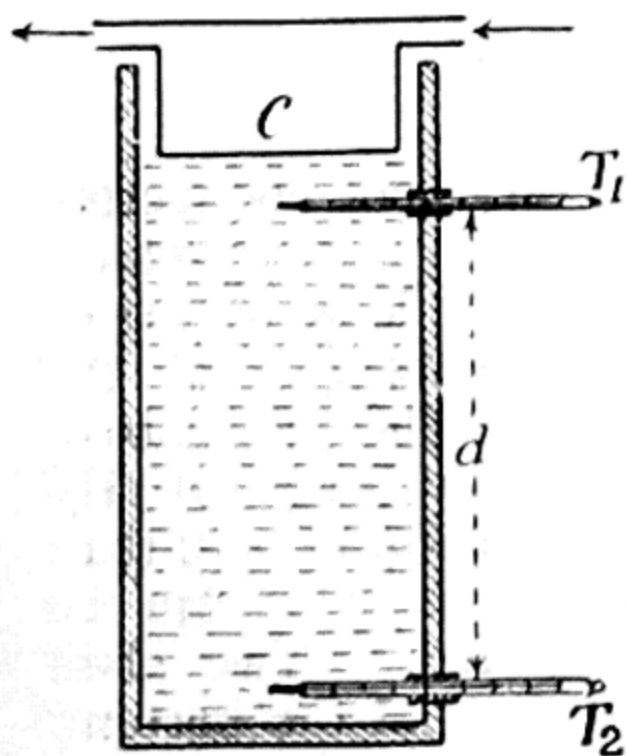


Fig. 13.13.
K by Despretz method.

13.14. K for Liquids. When a liquid is heated from below, convection currents are set up in it and they carry the heat with them. The whole liquid mass is thus heated up. While studying conduction in liquids, all convection of heat must be avoided. This is done by supplying heat to the top-most layer of the liquid. Experiment shows that heat travels very slowly down the liquids i.e., liquids are poor conductors of heat.

In the experiments of Despretz and Bottomley the liquid was contained in a tall

wooden cylinder and two thermometers T_1 and T_2 were placed horizontally in the liquid, one near the top and the other near the bottom. The liquid was heated by pouring boiling water into a copper vessel floating on the top of the liquid. The chief difficulty in these experiments was that even after forty hours of continuous heating, a truly steady state was not reached.

Lee's arrangement:—Lee has used an arrangement similar to that for poor conductors, in the case of liquids. The slab S is replaced by a hollow ebonite ring containing the experimental liquid. The heating is done at the top as usual but a thin disc of a partially-conducting material is interposed between the heating coil H and the copper disc C_3 , to ensure a steady but *slow* flow of heat downwards. Since the thickness of the liquid layer is 2 or 3 mm. only, the steady state is quickly reached and the experiment yields very accurate results. C_1, C_2, C_3, C_4 are thin circular copper discs, P is a disc of poor conductor, L is the liquid and R an ebonite ring. H is the heating coil.

The current in H is started and when the steady state is reached, the temperatures θ_1 and θ_2 on either side of P , and θ_3 and θ_4 on either side of L are measured. The heat flowing per second across P is $\frac{K_1 A_1 (\theta_1 - \theta_2)}{d_1}$ where A_1 is its area of cross-section, d_1 its thickness

and K_1 its conductivity. The outside of the pile is polished over to reduce heat loss from the curved surface to a negligible amount. Hence all heat coming across P must flow across R and L . The amounts of heat flowing across R and L are respectively

$$\frac{K_2 A_2 (\theta_3 - \theta_4)}{d} \text{ and } \frac{KA (\theta_3 - \theta_4)}{d}.$$

$$\text{Hence } \frac{KA (\theta_3 - \theta_4)}{d} + \frac{K_2 A_2 (\theta_3 - \theta_4)}{d} = \frac{K_1 A_1 (\theta_1 - \theta_2)}{d_1}$$

from which K is calculated.

13.15. Conductivity of Gases.

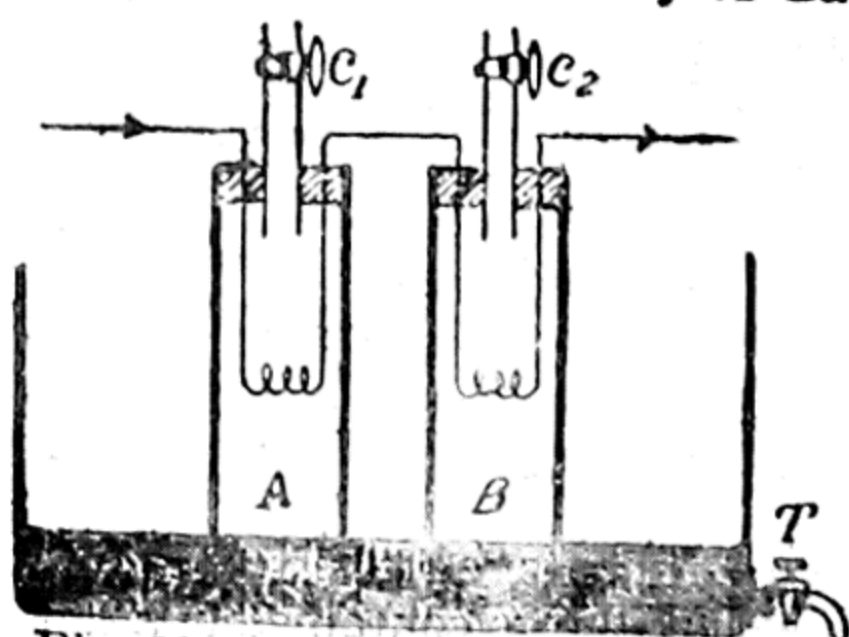


Fig. 13.15 Conductivity of Gases

Gases are very poor conductors of heat. The warmth of winter clothes is due to the large masses of air present in the texture of the cloth which serve as heat insulators. Hydrogen gas is a comparatively much better conductor of heat than air or any other gas. This can be easily demonstrated. Two glass tube A and B , open at the bottom, are placed in a glass trough containing mercury. Two heating coils of equal resistance are supported in

the tubes and the *same* current of electricity can be led through the two coils. To begin with, both the tubes are full of mercury. Mercury is made to flow out of the trough by opening the tap *T*. As the level of mercury falls, hydrogen is sucked into *A* and air or any other gas is sucked into *B* through tubes provided for the purpose at the top. The stop-cocks C_1 and C_2 are then closed and the current is started. The coil in *B* may be seen glowing while that in *A* does not glow at all although equal heat is being generated in both the coils. This is due to the fact that hydrogen conducts away the heat much faster than air.

The determination of the thermal conductivity of a gas is however difficult, as convection and radiation of heat also occur in gases. The experimental gas is confined between two metal plates placed horizontally and parallel to each other a few millimetres apart. The top plate which is surrounded by a guard-ring, is heated electrically.

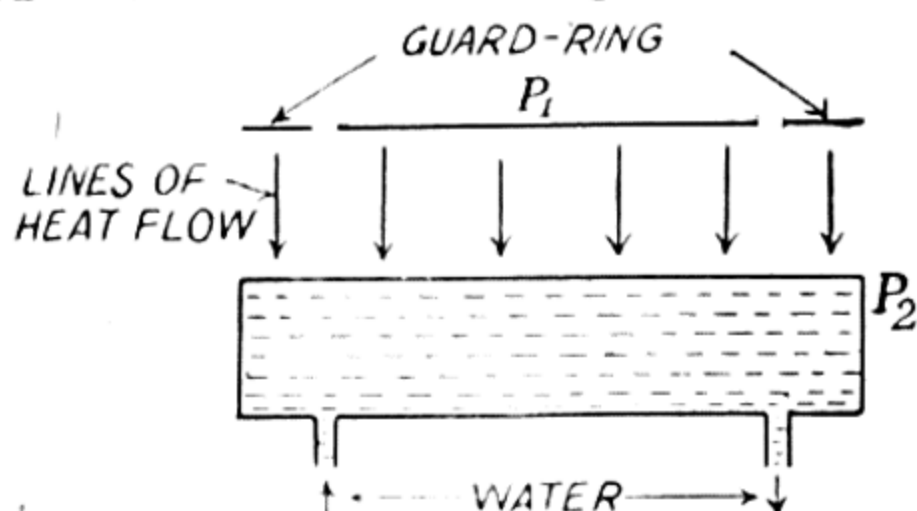


Fig. 13.16
K for gases

As the flow of heat is downwards, convection is automatically eliminated. To estimate the heat flowing directly by radiation from the top plate P_1 to the lower plate P_2 , the space between the two plates is exhausted. When the top plate is now heated, the lower plate will receive all the heat by radiation only. This can be easily calculated and allowed for. Gas is now admitted between the two plates and flow of heat started. After allowing for the heat received by radiation, the heat received by P_2 by conduction alone is determined. The heat received by the lower plate can be determined by circulating water at a constant rate behind it and determining the initial and final temperatures of the water.

If θ be the amount of heat flowing downwards per second by conduction alone

$$\theta = \frac{KA(\theta_1 - \theta_2)}{d}$$

when A is the area of the plate P_2 , and θ_1 and θ_2 the temperatures of P_1 and P_2 .

At very low pressures the conductivity of a gas is found to decrease with pressure. At such low pressures, the molecular mean free path becomes large and collision between molecules become very rare and as a consequence the heat transfer slows down.

The **Pirani pressure gauge** depends upon the above fact. In it, a constant current flows through a lamp-filament. The filament attains a steady temperature and hence a constant resistance. The value of this resistance depends upon the loss of heat through the gas by conduction, and therefore, upon the pressure of the enclosed gas. When the pressure falls, the conductivity diminishes. The

temperature and therefore the resistance of the wire increases. From the change in the resistance gas-pressure can be calculated.

Conductivity of gases.

Gas	K	Gas	K
Hydrogen	31.8×10^{-5}	Oxygen	5.8×10^{-5}
Nitrogen	5.8	CO ₂	3.4
Air	5.8	NH ₃	5.2

13.16. Law of Wiedemann and Franz. It is well-known that substances which conduct heat readily are also good conductors of electricity and that poor conductors of heat are also poor conductors of electricity. Wiedemann and Franz showed that *at any given temperature, the ratio of the thermal and electrical conductivities for all metals is proportional to the absolute temperature, or*

$$\frac{K}{\sigma} = a.T,$$

where σ is the electrical conductivity, T the absolute temperature while a is a constant, which is the same for all metals. This law is only approximately true.

An explanation has been attempted by supposing that the free electrons in metals are responsible for both kinds of conductivity, but the deductions do not agree well with experimental results. It has been found that with falling temperature a no longer remains constant. It diminishes in value as the temperature falls.

Table to illustrate Wiedemann and Franz law :—The values of $k/\sigma T = a$ for some substances, at different temperatures are given. It will be seen that a is not quite constant even at one temperature.

Temperature substances	−170°C	−100°C	0°C	18°C
Copper	1.85×10^{-8}	2.17×10^{-8}	2.30×10^{-8}	2.32×10^{-8}
Silver	2.04	2.29	2.33	2.33
Zinc	2.20	2.39	2.45	2.43
Tin	2.48	2.51	2.49	2.47
Iron	3.10	2.98	2.97	2.99
Lead	2.55	2.54	2.53	2.51

13.17. Thermal Insulation. Man has found that substances like wool, fur and feathers provide barriers through which heat cannot pass easily. The problem of thermal insulation is not merely one of

finding poor conductors. Air is a poorer thermal conductor than many solids, yet a heated body left in open-air cools down rapidly by convection and radiation. Structures like fur, wool, hair and loose materials like saw-dust and sand, enclose multitudes of air-pockets, which are so small that they reduce convection almost to zero, while the many surfaces of fibres and grains act as reflectors and traps for much of the thermal radiation that would otherwise pass through.

To serve as an insulator, the material, in addition to being a poor conductor should have certain other properties. For high-temperature insulation, the material should not deteriorate at those temperatures, while for low-temperature insulation it should be damp-proof. For some purposes the material should have sufficient mechanical strength, while in other cases, it should be light or should be able to resist chemical action. It should be easy to use and what is more important should not be costly. The basic materials used for such purposes are :

- (i) Cork
- (ii) Asbestos
- (iii) Magnesium carbonate
- (iv) Diatomaceous silica
- (v) Glass wool
- (vi) Rock wool.

The last two are made by melting silica minerals in a furnace and pouring the molten mass in fine streams into a high-velocity jet of steam. The molten mass is blown into silky fibres which rapidly cool and solidify. The resulting wool-like mass resists chemical action, is incombustible and has a low thermal conductivity. For covering hot-pipes a mixture of 85% magnesium carbonate and 15% asbestos fibre—to give mechanical strength to the former—is used. This material has a low thermal conductivity, is light and can be easily cut and fitted and is not affected by steam and water leakage. It can be used upto 600°F. For temperatures 600°—1400°F calcined diatomaceous silica and asbestos are used. Asbestos felt is used when there is excessive vibration and rough usage. Felted rock-wool and glass wool supported by wire-netting can be used upto 1000°F and have the convenience that they can be easily wrapped.

For covering cold pipes the insulation must have an air-tight surface otherwise it will become defective by absorbing moisture. Joints are made water-tight with water-proof cement and cork insulation (made by compressing pure cork into moulds at high pressure and baking) is then applied. It is held in position by copper-covered steel wires. Rock wool mixed with water-proof cement is also applied. Hair-felt made by chemically cleaning and felting cattle-hair is specially used for protecting water-pipes from freezing. It is very useful for low temperature work. For block insulation, blocks of the above materials are used and the blocks are fixed to brick or concrete-walls. Flat sheets of the materials *e.g.* asbestos-sheets are

used for covering flat surfaces. Hair-felt sheets are used to provide insulation for refrigerators.

Sheets of aluminium-foil are used both for high and low-temperature insulation. The foil 0.0003 inch thick is furnished in smooth rolls and is crumpled with hands before being applied. Its low thermal conductivity is due to air-spaces in between metal layers and due to the shining metal surfaces which act as reflectors. To give it mechanical strength it is supported in suitable jackets. It is extremely light in weight and is useful for covering large flat or curved surfaces.

In the thermos bottle the protection against heat-flow is the evacuated space, offering little opportunity for either convection or conduction. The highly polished silver-on-glass walls reflect all radiations that attempt to go through them. Conduction through the glass supports of the enclosure is almost the only means the heat has, to enter or escape.

To secure the most effective thermal insulation in the laboratory, the usual method is to surround the body not necessarily by an insulating substance but by a medium which is kept at *precisely* the same temperature at which the body is to be maintained.

To sum up :

1. For *low temperature insulation*—cattle hair, wool, felt, cork and various combinations of these materials.

2. *Insulation for buildings etc.*—i.e. to cut down heat losses through walls and roof during winter and to prevent heat penetration during summer—cork, wool, wool slag and glass wool are the materials used. They can be used in blocks, in sheets or in special re-inforced batts. Metallic and reflecting type insulation is also used.

3. *Insulation for heating and process work.* (150°F to 300°F)—asbestos paper structures are used. They have low conductivity and cost little.

4. *Insulation for power-generation field.* (300°F to 600°F). On account of mechanical vibration, an insulation consisting of 85% magnesia and 15% asbestos is used. Asbestos sponge is also in the market.

5. *High temperature insulation.* (600°F to 1400°F) materials used are diatomaceous silica and asbestos, the former being an excellent material. Sometimes the two materials are mixed together.

6. *For High-temperature pipe-covering.* We use one layer of diatomaceous silica and one layer of 85% magnesia and 15% asbestos, the silica forming the inside layer.

QUESTIONS

1. Write short notes on Conduction, Convection and Radiation.
2. Deduce a definition of Thermal Conductivity. Describe the Forbes' method for determining K for a metal.
3. Describe Lees' method for the conductivity of metals. In what respects is it superior to the Forbes' method?

4. How will you show that crystals have different conductivities in different directions ?

5. Give a laboratory method for determining K for cardboard.

6. Discuss the flow of heat in a metal rod and explain the meaning of steady state and deduce the equation of heat-flow.

7. What difficulties are experienced in determining the conductivities of liquids and gases and how are they overcome ?

8. Outline a method for determining the conductivity of a gas. How will you show that hydrogen is a better conductor than air ?

9. Briefly explain Angstrom's method for determining the conductivity of a metal.

10. Write brief notes on

(i) Conductivity of earth's crust, (ii) Wiedemann and Franz' law, (iii) Practical application of conductivity determinations. (iv) Age of the earth.

11. Thickness of ice on a lake is 10 cm. and the temperature of air is -20°C . At what rate is the thickness of ice increasing ?

K for ice = $.004$, density of ice $.92 \text{ gm/cc}$.

L for ice = 80 cal/gm .

$[.0001087 \text{ cm/sec}]$

12. Explain the Lees method for determining the conductivity of poor conductors.

13. How will you determine the conductivity of rubber given in the form of a tube.

14. Give the Lee's method for determining the conductivity of liquids.

15. Write an essay on heat insulation and heat insulators.

CHAPTER XIV

RADIATION

If you have had your attention directed to the novelties in thought in your own life-time, you will have observed that almost all really new ideas have a certain aspect of foolishness when they are first produced.—*A. N. Whitehead*.
All we know is still infinitely less than all that still remains unknown.—*William Harvey*.

14.1. In the process of radiation heat travels directly from one body to another in straight lines without affecting the intervening medium. The rapidly oscillating molecules of the hot body create waves in the ether. The waves carry energy with them which they transfer to the comparatively slow-moving molecules of the colder body on which they happen to fall. The molecular kinetic energy of the latter increases in consequence and manifests itself in a rise of temperature. Heat travelling by radiation is called *radiant heat*. In general, its properties are similar to those of light.

1. Radiant heat can be reflected like light and obeys the laws of reflection.

1. It can be refracted using prisms and lenses of a material transparent to heat radiations *e.g.*, rock-salt.

3. It travels with the velocity of light.

4. It follows the law of Inverse Squares.

5. It shows interference, diffraction and polarisation effects like ordinary light.

The wavelength of the radiations constituting radiant heat is greater than that of the light-waves. The wave-length of the red rays is about 8×10^{-5} cm. while the infra-red rays constituting radiant heat may have a wave-length of the order of a fraction of a millimetre.

All bodies are not equally transparent to radiant heat. Bodies which transmit heat radiations freely are called *Dia-thermanous* while those which absorb them are called *Athermanous*. Generally bodies transparent to light are also transparent to radiant heat and vice versa, but it is not always so. Thus water in thin layers transmits light but effectively cuts off heat radiations while a solution of iodine in carbon-bisulphide though transparent to heat radiations is opaque to light.

No substance is perfectly diathermanous; air is nearly so. Rocksalt and sylvine are considerably diathermanous. All metals, wood, etc., are examples of athermanous bodies.

Again there are substances, which though diathermanous to one kind of radiation, are athermanous to other kinds. The radiations

from the sun can pass freely through glass and it remains cool, but glass effectively cuts off radiations from bodies which are not as hot as the sun is. In green-houses for plants, while the glass roof and walls freely admit heat radiated from the sun across them, they do not allow the heat radiated by the plants to go out. The plants are thus kept warm. This property of glass also makes it a valuable material for fire-screens. A glass fire-screen placed in front of a fire, absorbs most of the thermal radiations and becomes very hot.

14.2. Prevost's Theory of Exchanges. The sensation of heat experienced when we stand near a hot body can be explained by supposing that the hot body radiates heat to us, but the sensation of cold which we experience when we stand near a block of ice, cannot be explained unless we suppose that the ice emits cold radiations. To get over this difficulty Prevost suggested that all bodies whether hot or cold, are losing heat to their surroundings by radiation and are also receiving heat from them by the same process simultaneously. *The rate at which heat is emitted by a body increases with its temperature but is independent of the neighbouring bodies.* When we stand near a furnace we gain more heat from it by radiation and lose less heat to it and therefore feel the heat sensation. On the other hand, when we are close to ice, we lose more heat to it by radiation and gain less from it and hence have the feeling of cold.

Similarly when two unequally heated bodies are placed near each other in the same enclosure the hot body loses more heat to the cold body, but gains less from it. This exchange of heat goes on till they both come to a common temperature. The exchange of heat does not end abruptly at this stage. Both are still losing heat and gaining heat, but since their temperature is the same, the gain of heat exactly balances the loss. In other words, the equilibrium is dynamic.

14.3. Emission and Absorption of Radiation. The amount of heat lost per second by one square centimeter of a surface *at a given temperature* depends only on its nature. It can easily be shown that while dull black surfaces are very good emitters of heat radiation, bright polished surfaces are the worst.

In the Ritchie's arrangement, when the polished side P of a Leslie cube (which contains boiling water) faces the polished face P_1 of the thermoscope T and the black face B faces the black face B_1 , the liquid column sinks in II and rises considerably in I . This indicates a large absorption of heat in II . If, however, a polished and a black face oppose each other on both sides, the liquid column moves very little.

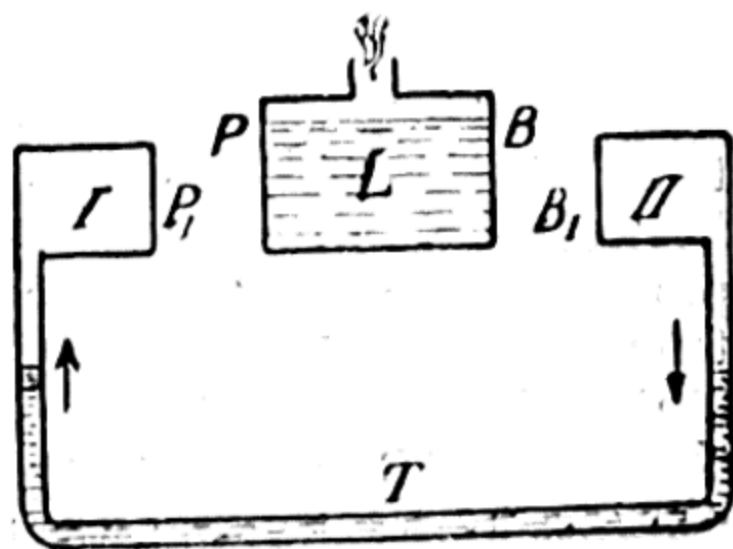


Fig. 14.1.
Ritchie's apparatus

In the first case, the black face of the cube emits a lot of heat, practically the whole of which is absorbed by the face B_1 of the thermoscope

while the polished face P gives out little and the face P_1 absorbs very little out of that. In the second case when the faces of the cube have been reversed the polished face of the cube emits very little radiation but it is completely absorbed by the face B_1 of the thermoscope, while, on the other side, the blackened face B emits a lot of heat which is mostly reflected by the face P_1 .

This shows that black bodies are good emitters and also good absorbers of heat while polished bodies are bad emitters as well as bad absorbers of heat *i.e.*, *good emitters are good absorbers of heat*.

14.4. Radiation in a Heated Enclosure. When a body is heated, it begins to radiate out heat. As the temperature of the body rises, its molecules begin to vibrate faster, *i.e.*, with a greater frequency and in accordance with the formula $v=n\lambda$, the body emits shorter and shorter wavelengths of radiation. If the body be a hollow enclosure, it can be shown that *the nature of the radiation and the amount of radiation per c.c. within the enclosure depends only on the temperature at which the walls of the enclosure are maintained. The radiation neither depends on the nature of the material of which the walls of the enclosure are made nor on the nature of the bodies that may happen to lie within it.*

Thus suppose two enclosures A and B whose walls are perfect heat insulators are joined by a connecting tube having a shutter S in it. The shutter is closed and the enclosures are heated to the same temperature T . If possible, suppose that the amount of radiation per c.c., *i.e.* the *energy density* is greater in A than in B . The shutter is opened for a short time and the two enclosures put in communication with each other. More radiation will leave A and go into B but less of it will travel in the reverse direction because energy density in A is the greater. The shutter is now closed and the two enclosures are allowed to adjust themselves to the new energy distribution. The energy density in A has diminished while its walls are still at their original temperature. They will, therefore, lose heat into the enclosure and cool down till equilibrium is again attained. On the other hand, the energy density in B is greater than before, hence its walls will absorb energy from within and get heated. This means that a difference of temperature will now be produced between A and B , although they were originally at one temperature. Work can be obtained by using B as the hot body of a heat engine and A as its cold body without supplying any energy to the system AB , and this is manifestly absurd. Hence the energy densities in A and B must be identical.

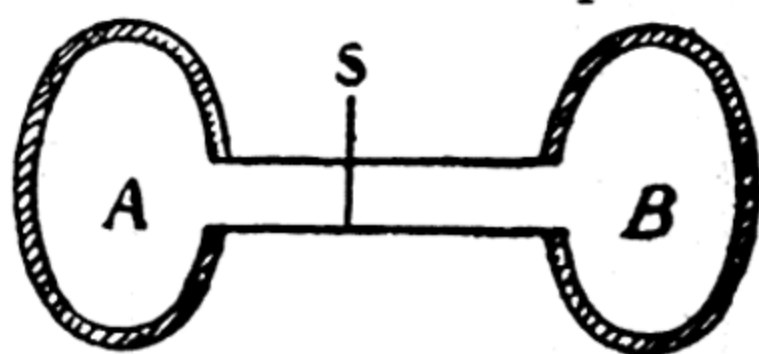


Fig. 14.2.
Uniform Temperature
Enclosures.

14.5. Kirchhoff's Law. The energy density of radiation in a uniform-temperature enclosure is uniquely determined by the temperature of the enclosure. A body placed in such an enclosure

ultimately takes up the temperature of the enclosure and becomes indistinguishable from it.

If e_{λ} be the emissive power of the body at the temperature of the enclosure, for wave-length λ , the total radiation lying between λ and $\lambda + d\lambda$ emitted by it per second is $e_{\lambda} \cdot d\lambda$, but the body is also absorbing heat from the walls of the enclosure. If dQ be the radiation incident on it and a_{λ} be its absorptive power, the amount of radiation absorbed by it per second is $a_{\lambda} \cdot dQ$. The remainder $(1 - a_{\lambda})dQ$ of the incident radiation will be reflected or transmitted. If $e_{\lambda} \cdot d\lambda$ be the amount of the heat lost by the body to the enclosure, the sum of the heats emitted, reflected (or transmitted) must be equal to the incident radiation, or

$$(1 - a_{\lambda})dQ + e_{\lambda} \cdot d\lambda = dQ$$

or
$$e_{\lambda} \cdot d\lambda = a_{\lambda} \cdot dQ.$$

or
$$\frac{e_{\lambda}}{a_{\lambda}} = \frac{dQ}{d\lambda}$$

and since
$$\frac{dQ}{d\lambda} \text{ is constant,}$$

$$\frac{e_{\lambda}}{a_{\lambda}} \text{ is the same for all substances.}$$

In other words, if e_{λ} is large for a substance, a_{λ} should be correspondingly greater, *i.e.*, good emitters of radiation are good absorbers of radiation also. Thus in the Kirchhoff's classical experiment, sodium vapour, when hot, emits the two yellow lines (D-lines) but cold sodium vapour absorbs these very lines. This selective absorption by a gas explains the existence of Fraunhofer lines in the solar spectrum.

If a polished metal ball with a spot of platinum-black on it be heated to a high temperature and then taken to a dark room, it is found that the dark spot which is a good absorber shines most. A coloured pattern on heated china will behave similarly when taken to a dark room. The pattern when cold is a good absorber, but when heated it becomes a good emitter, while the white china which is a bad absorber when cold, is a bad emitter when hot.

14.6. Black Body Radiation. A perfectly black-body is one which absorbs all the radiations, of whatever wavelength, that are incident on it. It neither reflects any of the incident radiation nor transmits it. Lamp-black is the nearest approach to such a black body and the radiating powers of various bodies are compared taking lamp-black surface as a standard.

Consider a heated enclosure with insulated walls, such that its walls can lose heat *only inwards*. Let a body be now placed in it,

If the body is hotter than the enclosure, it will lose heat to it and if cooler, it will gain heat from it till the body and enclosure come to a common temperature. The body will now be losing heat to the enclosure at exactly the *same* rate as that at which it is gaining heat from it. It makes no difference what the material or the colour of the body is and it is immaterial whether the body lies near to the walls or is in the middle of the enclosure. If the body is black, it will absorb practically all the radiations that fall on it and to restore the equilibrium it must radiate equally to the enclosure. If the body is highly polished, it will reflect back most of the radiations that are incident on it and will have to radiate out only a little just to make up for what it has absorbed from the incident beam. If the body is transparent, it will let through most of the incident radiation and will have to radiate out just a little. If the body happens to be coloured, it will absorb only a particular type of the radiation reflecting back strongly all other types. It is clear from the above discussion that although the different bodies radiate at different rates the quality and density of radiation in the enclosure remains unchanged. *The density of radiation in the enclosure is determined solely by the temperature of the enclosure and changes only with a change in temperature.*

It also follows from the above discussion that the *radiation from a uniform-temperature enclosure is identical with that from a black body at the same temperature.* Hence such a radiation is often spoken of as a **black body radiation**.

This conception of a full radiator has proved very useful in the theory of radiation. For practical purposes, a thick-walled hollow sphere with lamp-black interior and having a narrow circular hole on one side of it is taken as an enclosure. It is lamp-black on the interior to absorb any stray radiations that may fall on it through the hole. The sphere is heated electrically to any desired temperature and the radiations issuing out of the hole (which are black body radiations) can be measured with a sensitive bolometer (art. 14.7) or a radio-micrometer placed opposite the hole, care being taken that no heat falls on the instrument from the edges of the hole.

The radiations coming from a cavity in a clear coal-fire is almost black-body radiation. This accounts for the apparent indefiniteness of the surfaces of the glowing coals. The light coming to the eye from a cavity is independent of the nature of the surface of the coals and of its variations from place to place and is not determined by the nature of the surface at the particular point which is being viewed. Consequently the radiation entering the eye cannot convey an accurate impression of the nature of the surface

14.7. Measurement of Heat Radiations. A delicate instrument for *detecting* heat radiations is the **Boys' Radiomicrometer**, which is a combination of a thermo-couple and a delicate galvanometer. Two thin bars of antimony and bismuth have a thin blackened copper disc soldered at their outer ends while a loop of thin silver wire completes the circuit at the top. The whole arrangement is suspended by means of a quartz fibre between the pole-pieces

of a powerful horse-shoe magnet and is put in a thick case to protect it from stray radiations. When radiations fall on the copper disc, a thermo-electric current is produced and when it goes round the silver loop, the latter is deflected by the magnetic field. The deflection is indicated by a beam of light reflected by the mirror M (attached to the quartz fibre) on to a distant scale.

For measurement of radiations a **bolometer** is used. It consists of a number of exceedingly thin and narrow strips of platinum mounted close and parallel to each other on a slate frame and joined to each other in series. Two such sets are mounted in the adjacent arms of a Wheatstone bridge and are blackened to absorb the incident radiation and the bridge is balanced. One set is then exposed to the radiation-stream to be

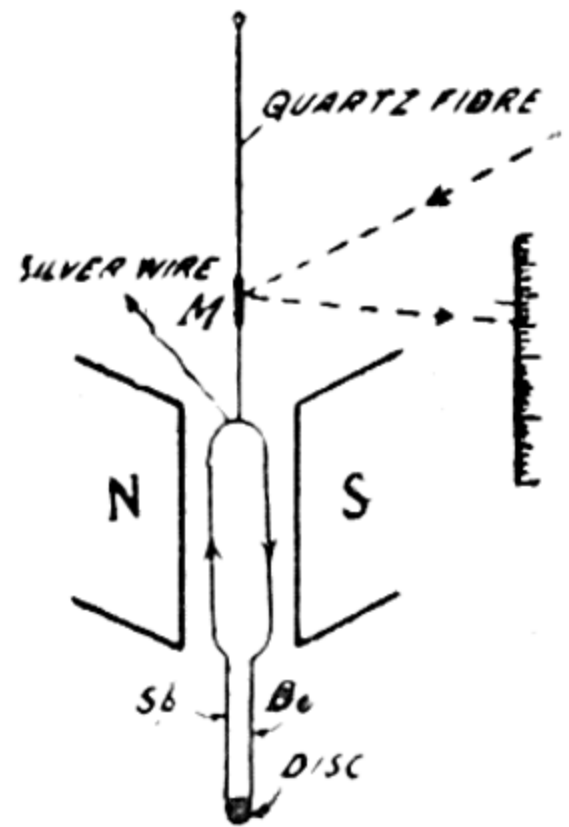


Fig. 14.3
Radiomicrometer

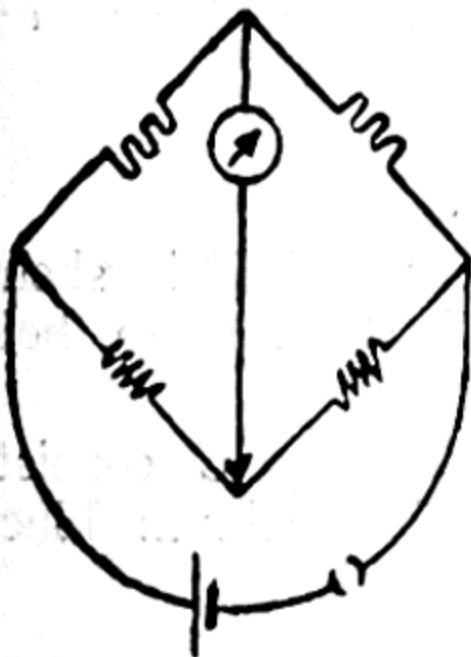


Fig. 14.4.
Bolometer.

measured, while the other is enclosed in a box to protect it from radiation. The resistance of the exposed strips increases and the balance is upset. *Since the rise of temperature is small*, the deflection of the galvanometer is practically proportional to the amount of radiation incident per second on it.

To measure the radiations contained in narrow strips of a spectrum a **line bolometer** i.e., one, in which the sets of platinum strips are replaced by single narrow strip, is used. If, however, it be required to measure the radiation in absolute units,

two thin strips of platinum, blackened on the surface, are joined at their backs to two junctions of a thermo-couple which includes a

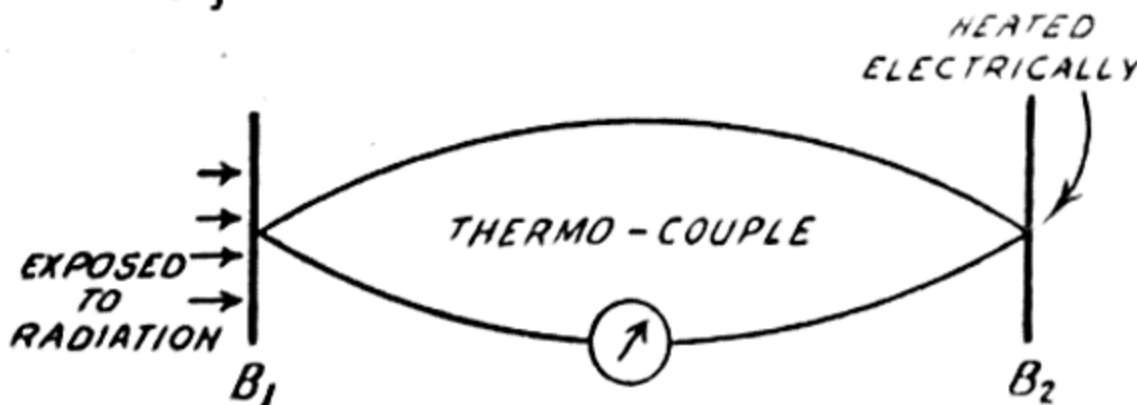


Fig. 14.5
Absolute Bolometer

sensitive galvanometer in its circuit. One strip is exposed to the radiation to be measured, while the other, which is protected from radiation, is heated electrically. The current through the latter is so adjusted that the galvanometer registers no deflection. This shows that there is no temperature-difference between the two strips and both are receiving energy at the same rate. The heat produced electri-

cally is EI Joules per second and is equal to the energy of the radiation beam.

The bolometer has a small thermal capacity and a high sensitivity. With it, changes in temperature as small as 0.000001°C can be detected. Bolometers are used in direction-finding by infra-red rays.

14.8 Stefan's Law. Newton's law of cooling, *viz.*, the rate of loss of heat from a body is proportional to the excess of its temperature over surroundings, holds good only for small differences of temperature. From the experimental data of Dulong and Petit, Stefan showed that *the total radiation from any heated body is proportional to the fourth power of its absolute temperature.*

Boltzmann, starting from thermodynamic considerations gave a theoretical proof of the law and showed that *it applies strictly to emissions from a black body only.* The **Stefan-Boltzmann** law may be enunciated thus :

If a black body at absolute temperature T is surrounded by another black body at absolute temperature T_0 , the amount of energy lost per second per square centimetre of the former is

$$E = \sigma(T^4 - T_0^4)$$

where σ is a constant, known as *Stefan's constant*.

Experimental Verification of the Law. Lummer and Pringsheim studied the emissions from a black body and found the law to hold correctly.

For temperatures from $200^\circ - 600^\circ\text{C}$ the black body C consists of a hollow copper sphere covered on the inside with platinum black

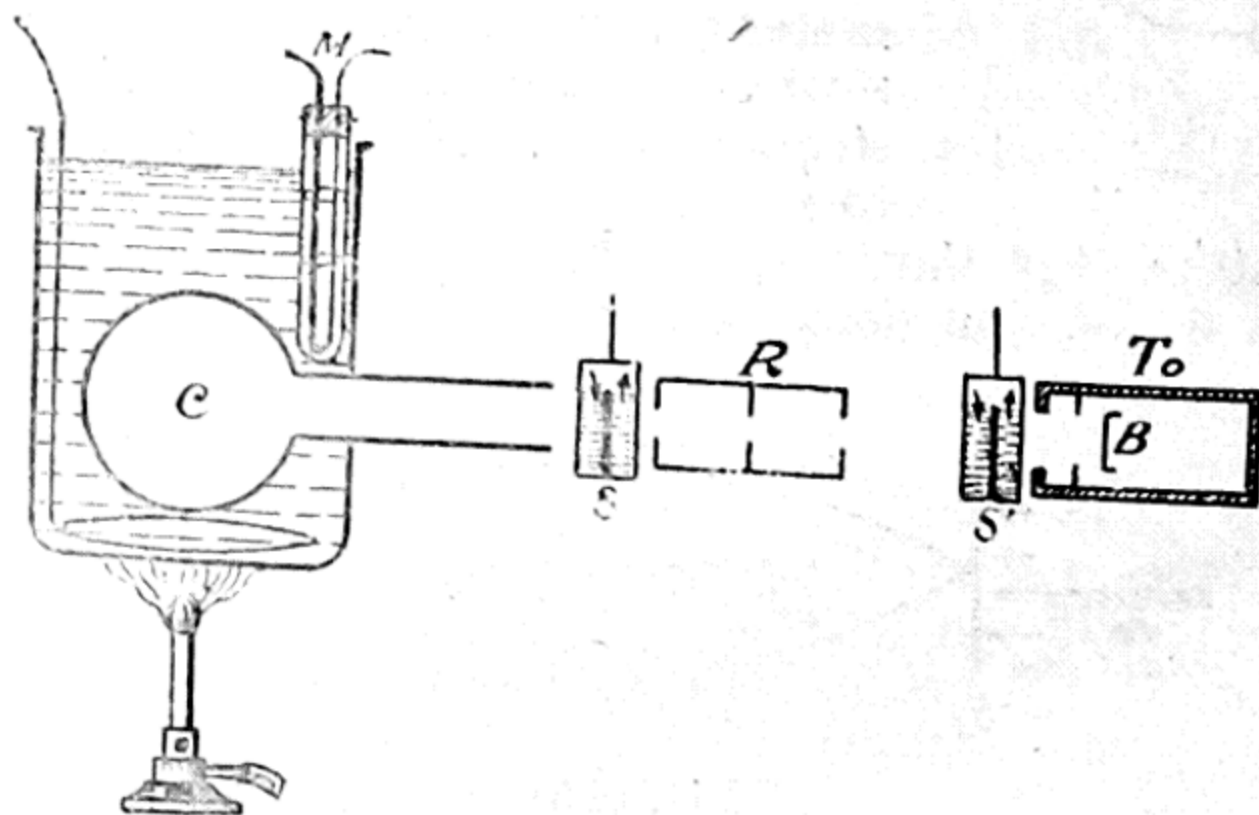


Fig. 14.6
Lummer and Pringsheim's arrangement

(to absorb any stray radiations that may enter C). It is placed in a bath of a mixture of sodium and potassium nitrates (which melts at 219°C). This salt bath can be maintained at any desired temperature within the indicated range and this temperature is measured with a thermo-electric thermometer M ,

For working at higher temperatures, the vessel was made of iron, blackened on the inside, but heated in a double-walled gas-furnace. The temperature inside the iron cylinder was measured with a thermoelectric thermometer which was enclosed in a porcelain tube that passed into C through the furnace.

S and S' are water-cooled shutters that intercept the radiations from C from falling on the surface of bolometer B , while R is a slit arrangement for getting a parallel beam of radiation.

The bath is raised to the desired temperature, which is then maintained steady, the shutters S and S' are raised to allow radiations from C to fall on the bolometer B which is surrounded by an enclosure at temperature T_0 . The maximum deflection of the galvanometer connected to B is noted. Observations are made by raising C to various known temperatures.

Let α denote the deflection of the galvanometer needle in any observation made at a temperature T of the vessel C and let T_0 be the constant temperature of the enclosure surrounding B . It is found that the ratio, $\alpha/(T^4 - T_0^4)$ is the same for all temperatures of C . As the deflection α of the bolometer is proportional to the energy E falling on it from the enclosure C , it follows that

$$E \propto (T^4 - T_0^4)$$

which verifies Stefan's Law.

14.9. Determination of Stefan's Constant, σ . The arrangement given in Fig. 14.6 was used but the bolometer B was replaced by an Absolute bolometer of the type depicted in Fig. 14.5 Strip B_1 was exposed to the radiation stream from the enclosure C while B_2 (which was protected from those radiations) was heated electrically so that there was no deflection in the connected galvanometer. The energy falling on B_1 was therefore equal to that generated in B_2 that is *e.i.* joules/sec. where e is the *P.D.* in volts acting across B_2 and i amperes is the current flowing through it.

In the relation

$$E = \sigma (T^4 - T_0^4),$$

$E = e.i.$ is therefore known, whence σ can be calculated. The value of σ found by Coblentz is

$$\sigma = 5.735 \times 10^{-12} \text{ watts}$$

14.10. Laboratory Determination of Stefan Constant, σ . A silver disc A of area A and of specific heat S is blackened over and placed on the table. To the bottom of the disc is attached one junction of a thermo-couple, whose other end is in melting ice, and a sensitive galvanometer is included in the circuit. The disc is covered over with asbestos sheeting. The cup C is now placed on the disc. The cup is blackened on the concave surface. It is heated on the outside with steam at temperature T . After some time, the asbestos is removed by turning the handle H and a series of readings of the galvanometer are taken every 30 seconds or so for 15 minutes and a graph between time t , and temperature T is plotted. This curve gives dT/dt .

If M is the mass of the disc, heat gained by it per second is

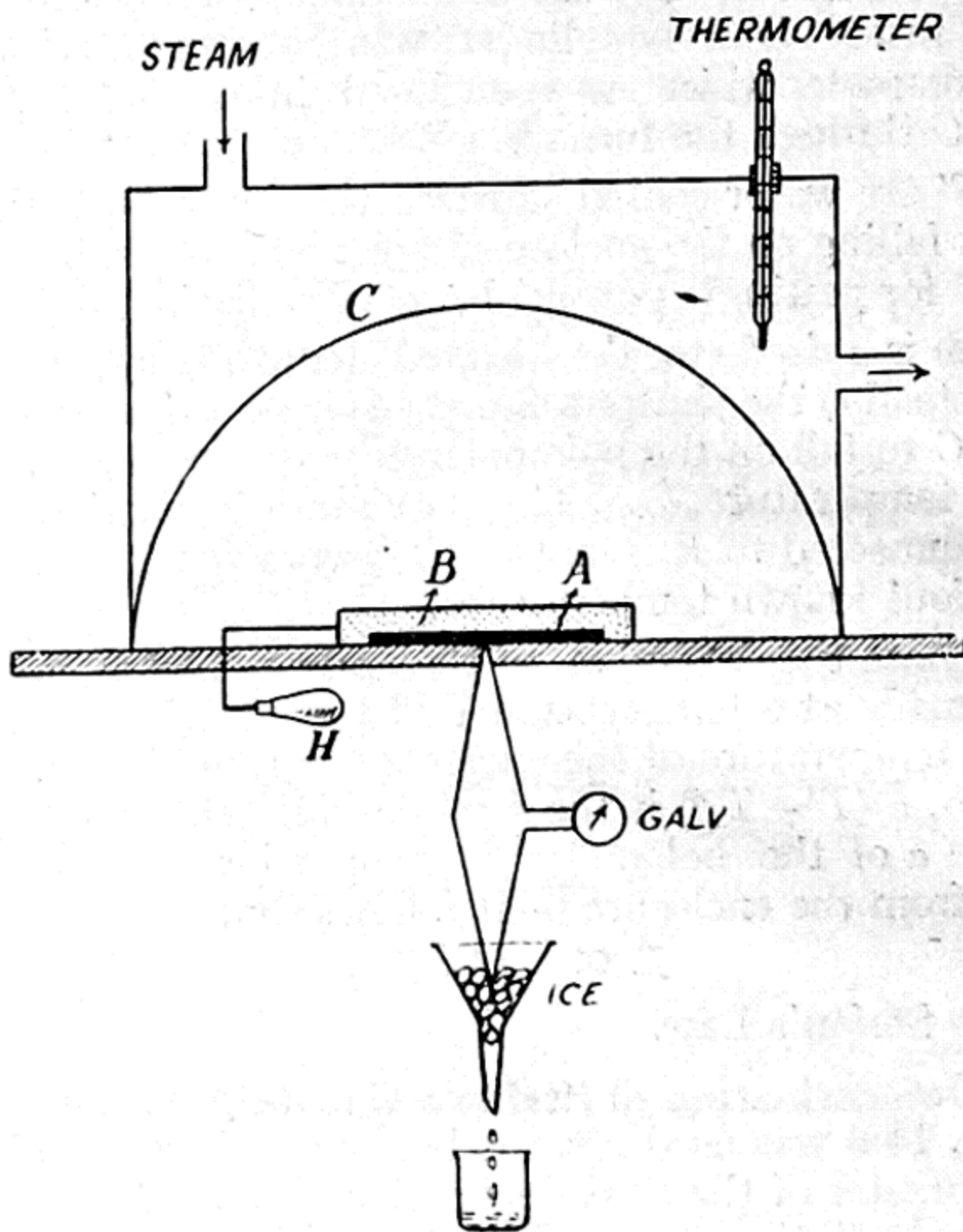


Fig. 14.7.
Stefan Constant.

$MS \cdot dT/dt$. If E_1 is the absorption of energy per second by the disc from the cup and E the corresponding loss by radiation,

$$MS \frac{dT}{dt} = \frac{E_1 - E}{J} \cdot A = \frac{\sigma A}{J} (T^4 - T_1^4) \text{ by Boltzmann Law}$$

and

$$\sigma = \frac{JMS}{A(T^4 - T_1^4)} \cdot \frac{dT}{dt},$$

where $J = 4.2 \times 10^7$ erg./cal., is the mechanical equivalent of heat and T_1 is the temperature of the disc. This last quantity is determined by calibrating the couple, so that from the deflection of the galvanometer, the temperature of the disc is known at once.

14.11. Distribution of Energy in Radiation Spectrum. It is well-known that solids and liquids begin to emit visible radiations when heated to a temperature of about 500°C . This emission of radiation is there even at lower temperatures—but it is of a wave-length which is too long to excite vision. As the temperature of the body is raised, it begins to emit waves of shorter and shorter length. The colour of the radiations is first reddish but changes to dull red, then to orange, to yellow and finally to white as the temperature of the body progressively rises.

The radiation spectrum can be obtained by passing the radiations through a slit S_1 on to a concave mirror M , which renders them

parallel and throws them on a rock salt or a quartz prism placed on the turn-table of a spectrometer. The emergent light is focussed by the concave mirror M_2 on to a line bolometer, placed behind the slit S_2 . The bolometer is connected to a sensitive galvanometer. The turn-table is slowly rotated so that one part of the spectrum after another is successively focussed on the bolometer. The intensity of each line is proportional to the galvanometer deflection and thus the whole radiation spectrum can be mapped out.

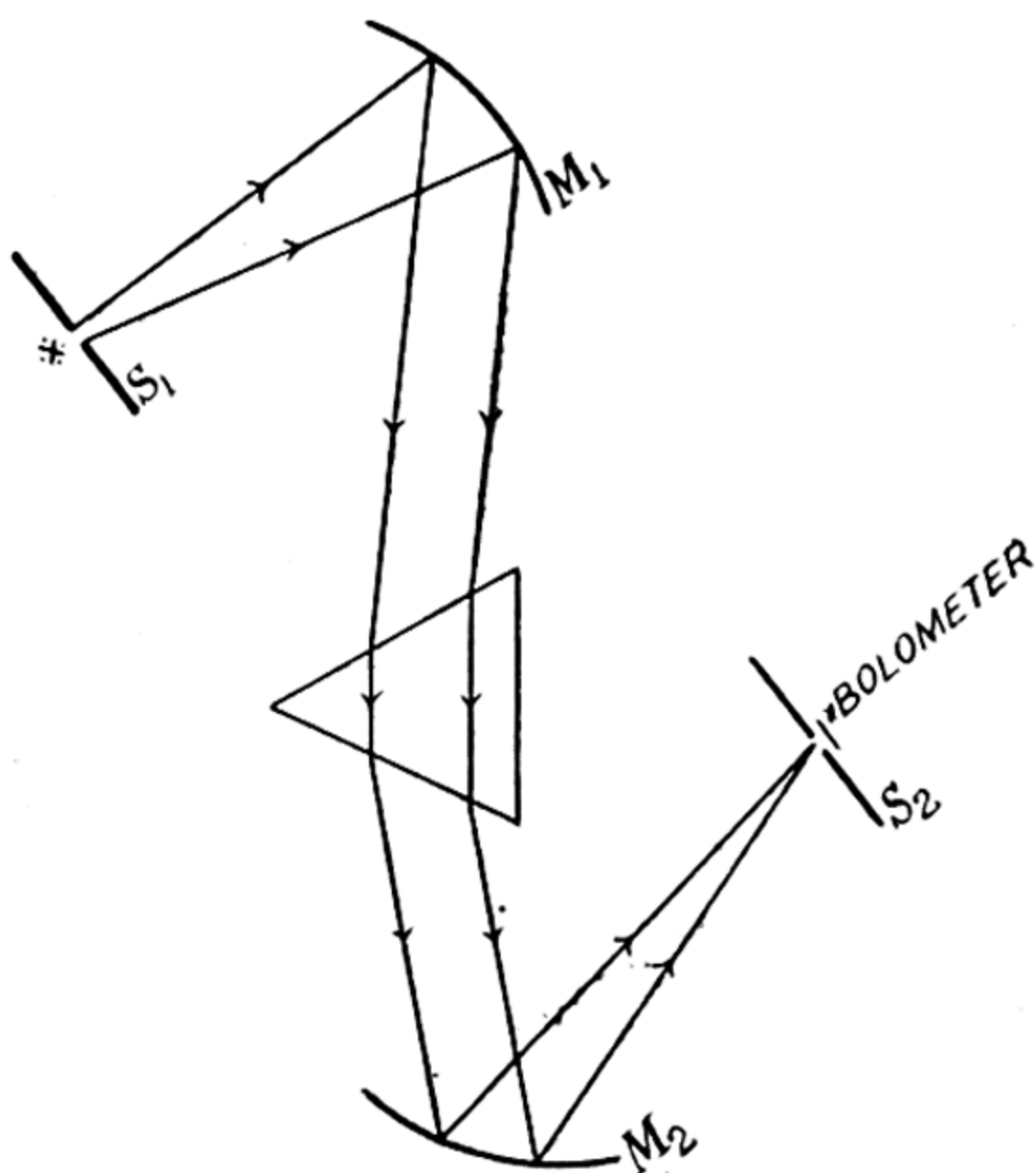


Fig. 14.8.
Radiation Spectrum.

It is found that energy is not uniformly distributed in the radiation spectrum.

As the temperature of the body rises, the radiation in every part of the spectrum at first increases rapidly. Then for a given temperature, the radiation is a maximum at some particular point in the spectrum. With a further rise in temperature this point of maximum radiation shifts towards the shorter wave-lengths. This means that the wave-length λ for which the energy emitted is a maximum decreases as the temperature rises, or

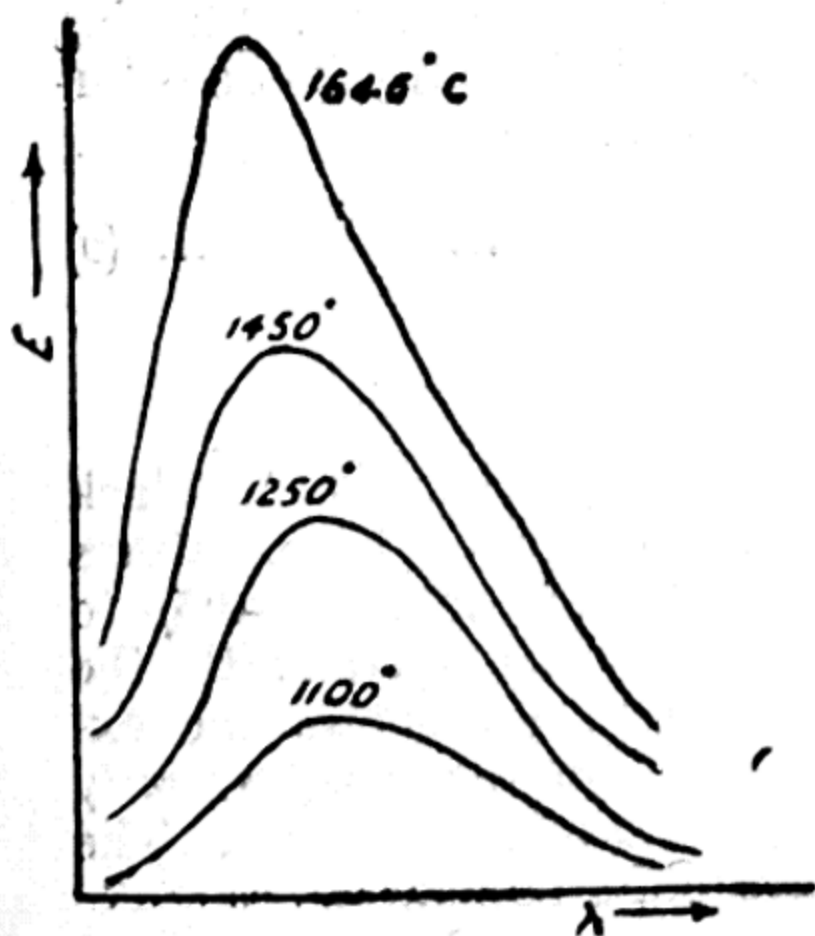


Fig. 14.9
To illustrate Wien's Law.

$$\lambda \propto \frac{1}{T}$$

or $\lambda T = \text{constant} \quad \dots (i)$

This is known as **Wien's Displacement Law**. The value of the constant in (i) was first obtained by Lummer and Pringsheim from the curves (Fig. 14.9) and was found to be 0.2884 cm. deg.

The area under each curve (Fig. 14.9) represents the total energy emitted by the body at that temperature. Evidently this area becomes larger and larger with increases in the temperature of the body. This area is found to increase as the fourth-power of the absolute temperature. Hence, the total energy

emitted by a hot body (black body) is proportional to the fourth power of its absolute temperature. This is **Stefan-Boltzman Law**.

Starting from thermodynamic considerations Wien showed that the actual amount of radiation at the maximum point is proportional to the fifth-power of the absolute temperature, or

$$E \propto T^5 \dots \dots \dots (ii)$$

Experimental determinations show that this law is true only at lower temperatures and for longer wave-lengths.

Again, Rayleigh and Jeans, starting from a consideration of the equilibrium of radiation in a cavity, proposed an alternative formula

$$E_{\lambda} \propto T.\lambda^{-4} \dots \dots \dots (iii)$$

for the energy distribution in the radiation spectrum, E_{λ} being the energy at wave-length λ for temperature T .

Experimental determinations show that this formula holds good only at higher temperatures and for shorter wave-lengths.

The fact that Wien's formula holds for longer waves only while the Rayleigh-Jean's formula holds for shorter waves only, leads us to suspect that the two might be only special cases of a more general law. The problem of distribution of energy in the radiation spectrum of a black body was solved by Planck in 1900. According to him, *exchanges of energy between ether and matter, instead of taking place continuously can occur only in discrete steps i.e., in multiples of some small unit, called the Quantum*. This quantum of radiation is called **Photon**. This quantum of energy, is not a fixed quantity, but is proportional to the frequency of radiation, ν , or

$$\epsilon = h.\nu \dots \dots \dots (iv)$$

where, $h = 6.55 \times 10^{-27}$ erg.-sec., is called Planck's constant. Starting from quantum considerations, Planck showed that energy is distributed in the radiation spectrum according to the relation

$$E_{\lambda} = c_1 \cdot \frac{\lambda^{-5}}{e^{\frac{c_2}{\lambda T}} - 1} \dots \dots \dots (v)$$

where c_1 and c_2 are constants.

This law reproduces the actual energy distribution for a black body in a very accurate manner. For a wide range of temperatures -300°K to 1700°K , and for a wide range of wave-lengths— 0.5μ to 52μ , ($\mu = 10^{-5}$ m.m.), this formula gives results which agree with the observed values to within one per cent. Formula (v) shows and experiment confirms that the *radiation spectrum contains comparatively little energy in the region of very short and very long wave-lengths*. The energy is mostly concentrated in the intermediate region.

Now, if Planck's law is correct, it must reduce to Wien's law and to Rayleigh-Jean's law for the ranges in which they hold.

(a) If λT is small i.e. less than one (c_2 has a value $= 1.432$ cm.-degree), $e^{\frac{c_2}{\lambda T}}$ is > 1 , and neglecting 1 in the denominator, we have $E \propto \lambda^{-5}$,

As λT is constant, $T \propto 1/\lambda$

$$\therefore E \propto T^5,$$

which is Wien's law.

(b) If λT is large, $e^{c_2/\lambda T}$ can be expanded into a series which easily gives

$$E \propto \frac{\lambda^{-5}}{c_2/\lambda T}$$

or

$$E \propto T \cdot \lambda^{-4}$$

which is Rayleigh-Jean's law.

Formula (v) thus embraces (i) and (iii) as special cases.

It must be stated that the energy contained in a photon is very very small. Thus a photon of radiation, of wave-length $\lambda = 10,000$ A.U. (1 A.U. = 10^{-8} cm.) contains only 2×10^{-12} ergs. *Heat radiation is so fine-grained that for all practical purposes it may be taken as continuous.*

14.12 Production of High Temperatures. Flames afford a simple and convenient method for obtaining high temperatures. The temperature at the top of the Bunsen flame is about 1540°C , while that in a Mecker burner (in which a wire gauze is provided at the top of the Bunsen burner) the temperature is about 1640°C . By burning a mixture of one part of methane and two parts of oxygen in an atmosphere of oxygen a temperature of 2850°C can be reached, while by burning a mixture of equal volumes of acetylene and oxygen in an atmosphere of oxygen 3100°C can be obtained. The Langmuir atomic hydrogen flame provides a temperature of 3800°C . In the last arrangement, molecular hydrogen is circulated round a tungsten electrode of an electric arc where it is dissociated. Recombination occurs in the flame with the evolution of heat. These flame furnaces are designed to direct the flame on the sample (where this is possible) to minimize heat losses but certainly they have not the ease of control of electric furnaces.

Electric furnaces. (1) *Carbon-granule furnaces* utilize the heating effect of a current conducted between two electrodes through pulverised carbon placed around the specimen. Uniformity of temperature is poor because the current follows the path of least resistance, which therefore is the region of the highest temperature.

(2) *Wire-wound furnaces* use nichrome resistors upto 1100°C and platinum resistors upto 1400°C . The heat transfer is facilitated by the use of thick wire wound on the inside of a magnesia cylinder.

(3) *Rod furnaces* use rods of recrystallized silicon carbide which radiate directly into the volume to be heated. It can be used upto 1500°C . Since heat is radiated from a small surface, care must be taken in designing the furnace to secure a uniformity of temperature.

(4) *Arc furnaces* are very useful and most convenient for concentrating a large amount of heat into a small volume. Temperatures of 3000°C can be easily maintained in the industrial type of furnaces, where they are used for manufacturing calcium carbide and steel.

In the laboratory, they are used for melting the oxides of manganese, zirconium and thorium.

(5) *High-frequency Induction furnaces* consists of a solenoid producing an alternating magnetic field which can develop, by induction, a current in a conducting substance of any shape placed inside it. The uniformity of temperature is best when the sample is a liquid metal. Electrical non-conductors (refractory oxides) are surrounded with a conducting cylinder of tungsten or graphite and heated indirectly. Conditions of highest purity are attainable here.

It may be remarked in passing that

- (i) *Molecules break up* at temperatures between 10^3 — 10^4 °K.
- (ii) *Atomic shells break up* at temperatures between 10^4 — 10^6 °K.
- (iii) *Atomic nuclei break up* at a temperature of 10^9 °K.

In order to obtain complete thermal dissociation of matter, that is to break up the nuclei themselves into separate nucleons (*i.e.* into protons and neutrons) the temperature must go up at least several billion degrees. Even in the hottest of stars we do not find such high temperatures.

14.13. Measurement of High Temperatures. Temperatures upto about 250°C can be measured with an ordinary mercury thermometer. Using gallium (M.P. 29.7°C and B.P. 1600°C) as liquid and fused quartz as the material for the bulb and the capillary tube, temperatures upto 1000°C have been measured. Northrup measured temperatures upto 1680°C with a graphite thermometer using molten tin (M.P. 231.8°C and B.P. 2260°C) as liquid.

Hydrogen thermometer cannot be employed for temperatures beyond 500°C because the platinum bulb becomes porous to hydrogen which is therefore replaced by nitrogen. Using a bulb of rhodium, temperatures upto 1600°C can be measured. The internal rise of pressure, however, begins to give trouble at high temperatures because the material of the bulb softens and the volume of the bulb tends to increase. This renders temperature-measurements less trustworthy.

Platinum thermometer is quite reliable upto 1000°C while a platinum and platinum-rhodium couple can be used upto 1600°C and is quite convenient to use. Beyond 1600°C , Radiation Pyrometers must be used.

Temperatures of very hot bodies can be judged roughly by their colour or brightness.

Lowest visible red	...	temperature	470°C
Dull red	...	"	600°C
Cherry red	...	"	700°C
Light red	...	"	850°C
Orange	...	"	900°C
Yellow	...	"	950 — 1000°C
White	...	"	1150°C and above

14.14 Radiation Pyrometers. It will be seen that in all the types of thermometers so far described *the bulb of the instrument* has to be placed in contact with the hot body and when the bulb begins to soften, the instrument becomes useless as a temperature measurer. Here-in lies the chief merit of the radiation thermometers, for they have not to be placed touching the hot body. They can therefore measure any and every temperature no matter how high it may be. Their use is confined to the measurement of temperature of those bodies which are hot enough to radiate out heat in measurable quantities. Their range roughly begins at about 600°C and there is no upper limit to the temperatures which they can measure. Since the radiation formula holds correctly for black bodies only, the more a source corresponds to a black body, the more correctly will its temperature be indicated by the radiation thermometer or radiation pyrometer, as it is called.

14.15 Fery's Radiation Pyrometer.

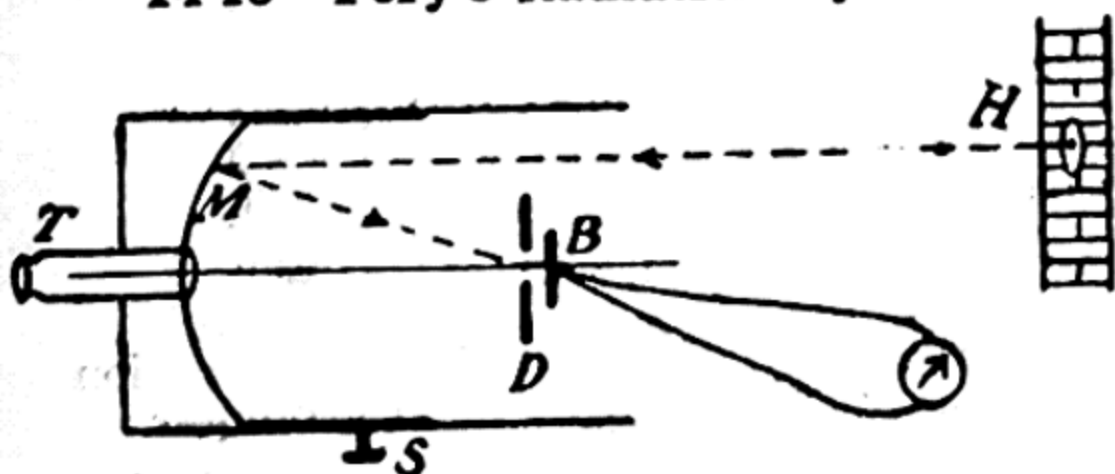


Fig. 14.10

Fery's Radiation Pyrometer

It is based on the Stefan-Boltzman Law. It consists of a concave mirror M , placed at the end of a metal tube which also carries a diaphragm D having a circular aperture at its centre. The radiations coming through a hole H in a wall of the furnace whose temperature

is to be measured, are focussed by the mirror M on the aperture in the diaphragm. For this purpose M can be moved relative to D by means of a thumb-screw S . The correctness of focussing can be judged by looking through a telescope T fixed in a hole provided in the middle of the reflecting surface, for the purpose. Passing through the diaphragm the radiation falls on a blackened disc B , to the back of which one junction of a thermo-couple is soldered. *Provided the image of the furnace-hole completely fills the aperture of the diaphragm,* the reading of the galvanometer included in the thermocouple circuit is independent of the distance of the instrument from the hot body. Thus when the distance of the instrument from the furnace is doubled, the radiation falling on it diminishes to one-fourth, in accordance with the Inverse Square Law. The diameter of the image also becomes one-half and its area becomes one-fourth, so that the radiation falling on unit area of the image per second remains undiminished. This is a great convenience and we can set the pyrometer at any convenient distance from the source.

The deflection of the connected galvanometer is proportional to the energy falling on it and in accordance with Stefan's law, $E = \sigma T^4$. This enables us to calculate the temperature. The usual method however, is to sight the pyrometer on a hot body at known temperatures and get a calibration curve and to read unknown temperatures from the curve. We obtain better results in this way.

14.16. Fery's Absorption Pyrometer. A comparison is made between the red rays emitted by a standard electric lamp and the red rays emitted by the hot body whose temperature is being measured.

The radiations from the hot body fall normally on a wedge of red glass P_1 . By sliding a similar wedge P_2 , a parallel-sided plate of variable thickness is introduced in the path of the incident radiation. The beam goes straight through the glass plate G down the tube. At the same time, red light from a standard lamp L is reflected down the tube by a small silver strip attached to the back of G and the two beams are seen by an eye placed at O . The position of P_2 is adjusted till the field appears of one uniform brightness. The efficiency of absorption of the glass wedges P_1 and P_2 being known, the temperature can be directly calculated.

This instrument is specially useful for measuring the temperatures of bodies which, though very hot, are small in size.

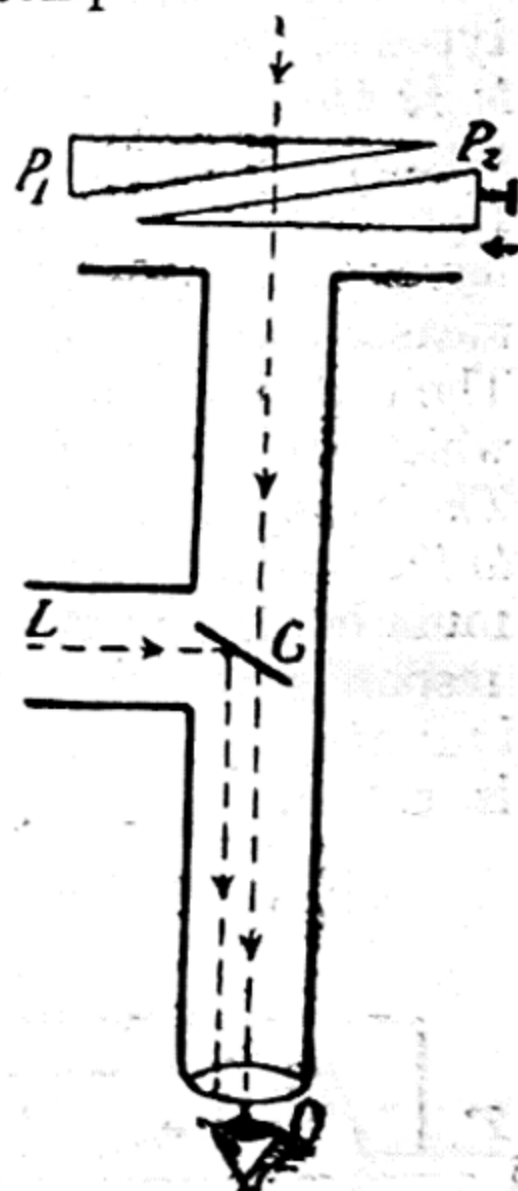


Fig. 14.11
Fery's Absorption
Pyrometer

14.17. Disappearing Filament Pyrometer. This instrument is due to Holborn and Kurlbaum. The intensity of red part of the spectrum of the radiations emitted by a hot body is compared and matched with that given out by the filament of a small electric lamp. The image of the source S is focussed by a lens L on the straight thin filament D of a low-voltage incandescent lamp. A lens E which forms the eyepiece of the telescope of which L is the objective is now focussed on the filament. The eye is placed behind a plate of red glass G which allows only a narrow band of wavelengths to pass through it. The eye sees an image of the filament super-imposed upon an illuminated background. The current through the filament is now adjusted till the contrast between it and the image of S just disappears and the filament becomes invisible against the back-ground. Since the two are now

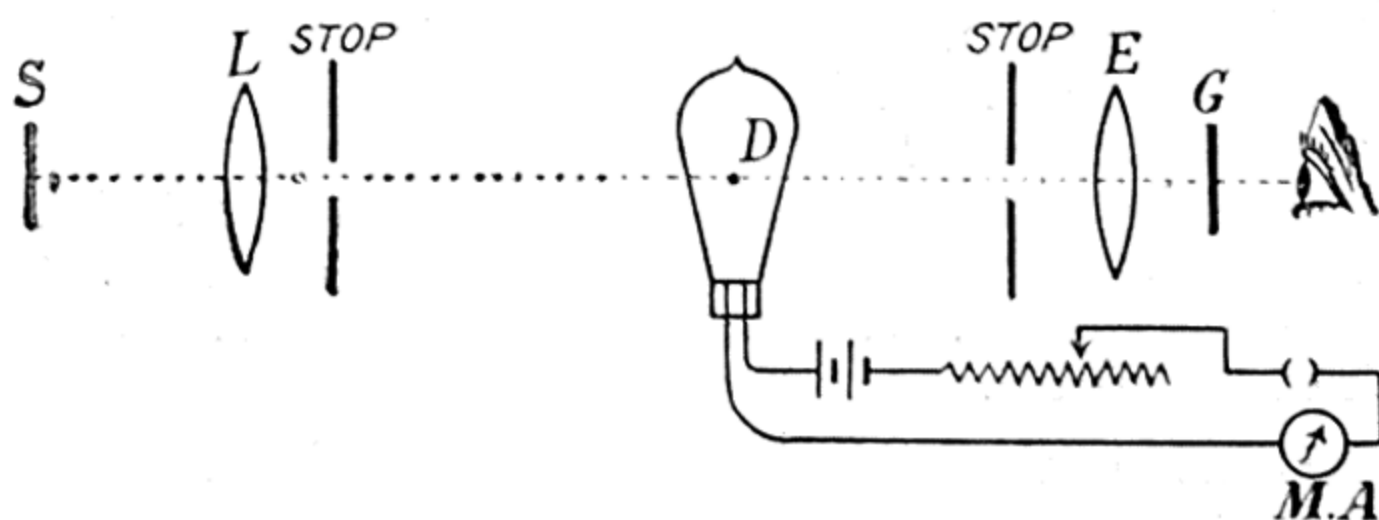


Fig. 14.12.
Disappearing-filament Pyrometer.

equally bright, they must be emitting equal amounts of energy per second and hence must be at the same temperature.

The instrument is calibrated by sighting it on the hole of a constant-temperature enclosure which is heated to various known temperatures that are measured with a standard couple. The current through the filament is also measured at each stage. A potentiometer may be used if extreme accuracy is required. The current-strength used is from 20→60 milli-amperes. A curve is plotted between the current and temperature and unknown temperatures are read off the curve. The lamp should have a very clear glass bulb and should preferably have clear glass widows on both sides. The widows should not be perpendicular to the axis of the telescope but should be mounted at an angle of 15° from the perpendicular so as to avoid reflecting the images of the filament into the field of view. The vacuum in the bulb should be the best obtainable. The filament should preferably be of tungsten, because such a filament has a very long life.

14.18. Temperature of flames. Light from an incandescent tungsten foil A is directed through the flame on the blackened disc D of a radiation pyrometer. The current through the foil is adjusted till the deflection of the galvanometer remains constant whether the flame is interposed or removed. The temperatures of the filament and the flame must therefore be equal. The temperature of the

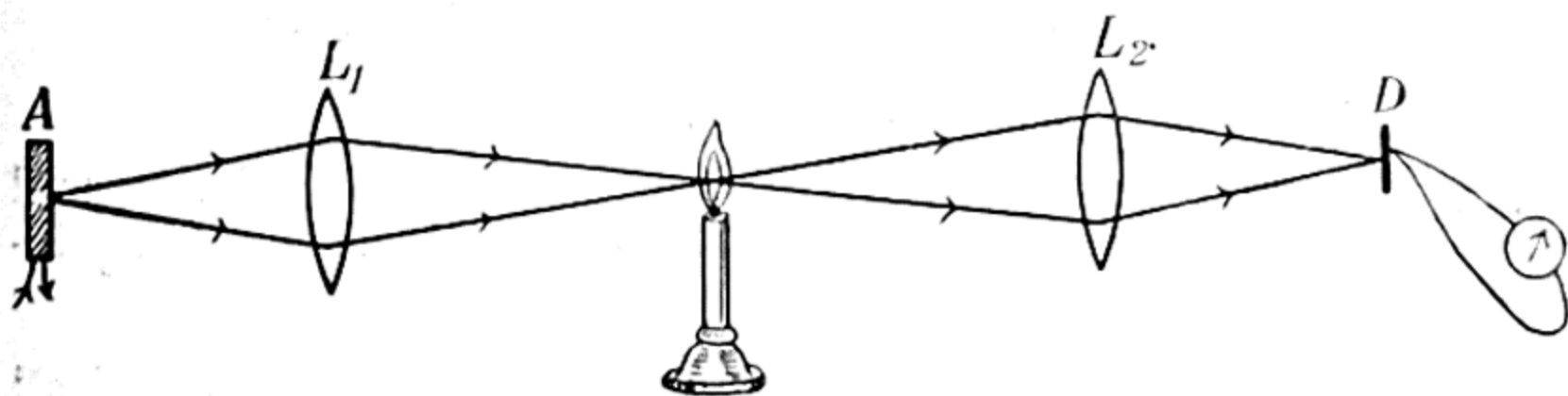


Fig. 14.13.
Temperature of flames.

foil is determined from a calibration curve, between temperature and the current flowing through the foil.

If the flame be non-luminous it is coloured with sodium. The light after passing through L_2 falls on the slit of a spectrometer. The temperature of A is adjusted till the sodium lines match the back-ground illumination. The temperature is then determined as above.

14.19. Temperature of the Sun. The sun is an intensely hot body whose central temperature exceeds 20 million degrees and whose surface temperature is about 6000°A . The surface temperature can be calculated by measuring the **Solar Constant** i.e., the radiation that would fall per minute on one square centimetre of the earth's surface held normally to the sun's rays, provided there were no atmospheric absorption.

In the Pouillet's pyrheliometer, a slow stream of water flows continually at the back of a thin, circular, blackened, metallic disc which is held normally to the sun's rays. Knowing the rate of rise of temperature and the quantity of water flowing past the disc per

minute, the solar constant can be determined. It is about 2.3 calories per square centimetre per minute.

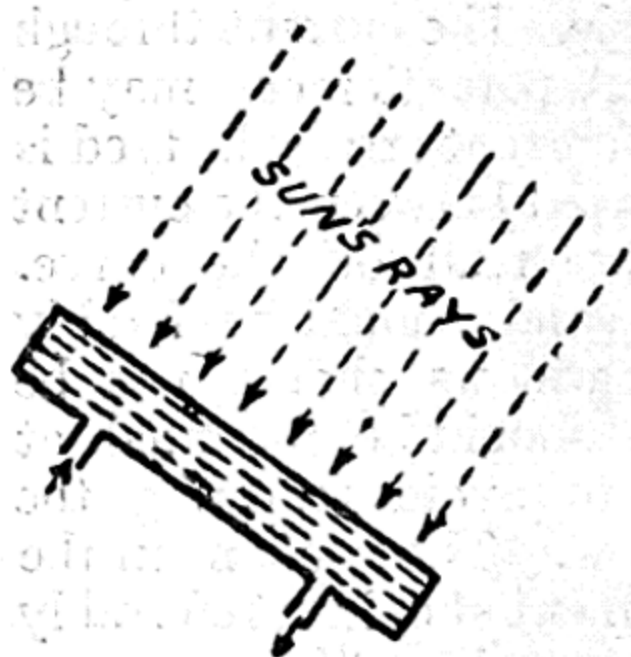


Fig. 14.14.

Principle of Pouillet's pyrheliometer.

If a sphere be drawn with the sun as centre and with the mean distance of the earth from it as radius, the total radiation falling on the surface of this sphere per minute is

$$2.3 \times 4\pi \times r_1^2$$

where r_1 is the mean radius. All this radiation has been emitted by the surface of the sun. If r_2 be the sun's radius, its surface area will be $4\pi r_2^2$. Hence the radiation E emitted by one square centimetre of the sun's surface per minute is

$$E = \frac{2.3 \times 4\pi \times r_1^2}{4\pi r_2^2}$$

Substituting the values of r_1 and r_2 , $E = 1.08 \times 10^5$ calories. To determine the surface temperature of the sun, apply Stefan's Law: i.e., $E = \sigma T^4$

$$\text{or} \quad 1.08 \times 10^5 = \frac{(5.735 \times 10^{-12})}{4.2} \times 60 \times T^4$$

whence

$$T = 6028^\circ\text{A.}$$

(We have divided σ by 4.2 to convert the watts into calories and multiplied by 60 to get the result per minute because E is the radiation emitted per minute.)

14.20. Source of Solar Energy. The sun is the supporter of all life on the earth and is the ultimate source of all activity. It is a giant sphere of intensely hot gas, of diameter 864,000 miles and is situated about 93 million miles away. It is 333,434 times heavier than the earth.

The earth collects only a small fraction of the total energy radiated out by the sun. The largest part of it is lost into inter-stellar space. Even so, the solar energy falling on the earth's surface equals 4,690,000 H.P. per square mile. The sun has been radiating energy at this tremendous rate continuously during its life of 2 billion years and the supply seems inexhaustible. Had the sun consisted of coal and the right amount of oxygen, the combustion of the entire material would have supplied the energy for only 2500 years. *What, then, is the source of energy in the sun?*

According to Helmholtz, the sun began its life as a giant sphere of cool gas with a diameter very much larger than its present diameter. Such a sphere could not be in a state of equilibrium, because the comparatively slight pressure of a cool and highly rarefied gas could not balance the mutual gravitational attraction of its various parts. The sun therefore, began to contract rapidly under its own weight, compressing the gas in its interior. This caused a heating up of the inner gas and was accompanied by a rise in its pressure also.

When the pressure of the gas in the interior became great enough to hold up the weight of the outer layers, further contraction of the sun stopped.¹ The sun could have come to a perfect equilibrium if there were no loss of energy from its surface. Owing, however, to the continuous loss of energy by radiation, the equilibrium would be upset and contraction continue.

Even if we assume that the initial size of the sun was infinite, the total energy liberated by it in shrinking to its present size would be only $\frac{1}{1000}$ of the energy which the sun has *actually* emitted so far.

Hence it appears that the Helmholtz's *contraction hypothesis* accounts correctly only for the early stages of the sun's evolution, but that in its present state the sun possesses other energy-sources much more powerful than those of chemical and gravitational origin.

It is now well known that the nuclei of atoms can be smashed by α -particles emitted by radio-active substances or by accelerated protons or better still by fast-moving neutrons, with the liberation of considerable amounts of energy. Aitkins and Houtermans (1929) advanced the hypothesis that "at the very high temperatures obtaining in the interior of the sun, the kinetic energy of the thermal motions becomes so great that the violent mutual collisions among irregularly moving particles of matter are as destructive of the nuclei as are the impacts of the atomic projectiles in the ordinary bombardment experiments. In fact, at the temperature of 20 million degrees, the kinetic energy of the thermal motion equals the energy of the atomic projectiles. At these high temperatures, matter no longer consists of atoms and molecules. The atoms are all stripped of their electronic shells. Bare nuclei and electrons move irregularly about. As the nuclei are not protected by electronic shells, violent collisions between nuclei lead to results fatal for them and the persistency of thermal collisions makes the thermo-nuclear reactions infinitely more effective than the ordinary bombardment process."

According to Bethe and Weizsacker the thermo-nuclear process mainly responsible for the energy production of the sun is a closed circular chemical reaction, the participants being the nuclei of Carbon and Nitrogen together with the thermal protons (*i.e.* nuclei of Hydrogen) with which they collide. Hydrogen is present in the Sun in very great abundance. The net result of the reaction-chain is the formation of one Helium-nucleus from four protons (or nuclei of Hydrogen) with considerable evolution of energy. "*The source of solar energy is the conversion of Hydrogen into Helium in the Sun's interior, the transformation being induced by the high temperature prevailing there and aided by the catalytic action of Carbon and Nitrogen (which are not consumed in the process and are recovered in 10^{14} years.)*"

¹ The pressure in the central regions of the sun reaches the tremendous value of 10 billion atmospheres. Under this pressure, the density of the gas is six times that of mercury (=78) and the temperature at the centre is 20 million degrees. At the surface of the sun, the corresponding values are 0.001 atmosphere, 10^{-16} gm/c.c. and 6000°C.

According to another theory due to Bethe and Critchfield two protons combine to form a deuteron in about 100 billion years which at once changes into He_3 by capturing another proton. In another 30 million years He_3 combines with He_4 already present to form Li_7 . This combines with another proton to form two He_4 nuclei. Energy is emitted as in the carbon cycle by transforming into radiation the binding energy of the Helium nucleus. Salpeter (1953) has shown that in the sun about five-sixths of the heat is being produced in this way and carbon-nitrogen cycle is of minor importance.

14.21. Temperature of Stars. The radiation received from the stars is very insignificant because of their tremendous distances from the earth, hence the method of the pyrheliometer cannot be used in their case. Their temperatures are estimated in the following ways:—

(1) *Using Wien's Displacement Law.* By examining the colour of the light emitted by the various stars, we can form a fairly good idea of their surface temperatures, because with rising temperature, the maximum of radiation shifts towards shorter wave-lengths. It has thus been shown that the reddish stars are comparatively cooler while the bluish ones are very hot.

(2) *By Fraunhofer Lines.* These lines are due to selective absorption in the solar atmosphere. Such absorption also occurs in the atmosphere of stars. Now, *the relative absorbing power of different atmospheres depends to a very high degree on their temperatures.* The Fraunhofer pattern changes from star to star and enables us to estimate their temperatures.

14.22. Temperature of Planets. All the major planets—Jupiter, Saturn, Uranus and Neptune are very very cold. Their surface temperatures are -150°C or even lower. There can be no seas and oceans on their surface and no water-vapour in their atmosphere. It has been suggested that the clouds which obscure the sight of Jupiter's surface may be only condensed carbon dioxide or some other such gas.

The planet Mercury always presents the same face towards the sun and the temperature of this face is 350°C . Its other side is however very dark and very cold. Venus probably behaves in the same way. Hence life, as we know it on the Earth, is not possible on most of the planets. They are either too hot or too cold to sustain life.

QUESTIONS

1. Briefly explain Radiation of heat and distinguish between diathermanous and athermanous bodies.
2. Give an account of Newton's Law of Cooling. What are its limitations? How can the method be used for determining the sp. heats of liquids? Can the method be applied to solids and gases as well?
3. Write short notes on:—(i) Prevost's Theory of Exchanges (ii) Kirchhoff's Law (iii) Black-body radiation (iv) Stefan's Law (v) Wien's displacement law.
4. Show that the radiation in a uniformly heated enclosure depends on its temperature and on nothing else.

5. Give an account of the methods used for the detection and measurement of radiant heat.

6. Write a brief essay on the distribution of energy in the radiation spectrum of a black body. What contribution has been made by Planck to the problem?

7. Write an essay on high temperature measurements and point out the defects in the various methods of measurement? Wherein lies the superiority of radiation pyrometers?

8. Briefly explain the Fery's and Kurlbaum's methods of high temperature measurement.

9. What is Solar constant? How can it be determined? How does it help us in determining the surface-temperature of the sun?

10. How would you proceed to determine the temperature of the glowing filament of an electric lamp? What is your estimate of this temperature?

[Temperature of vacuum lamps is about 2100°C while that of the gas-filled lamps is about 2700°C .]

11. State and explain the laws relating to the amount of radiation and the temperature of the radiating body. Define (i) coeff. of absorption (ii) coeff. of emission, (iii) perfectly black body.

In an experiment, mass of water with water-equivalent of the calorimeter was 63 gm. and the surface area of the calorimeter forming the area of the radiating surface was 100 sq. cm. Rate of cooling was $0.25^{\circ}\text{C}/\text{sec}$. and excess of temperature over surroundings was 50°C . Find the coefficient of emission. (Punjab University)

Coefficient of absorptirn is the ratio between the amount of radiation absorbed by a surface and the total radiation falling on it.

Coeff. of emission or emissivity is the amount of radiation emitted by unit area of a surface in one second when the difference of temperature between the surface and the surroundings is 1°C .

Numerical. The fall of temperature per second = 0.25°C .

\therefore Heat lost per second by the calorimeter = $63 \times 1 \times 0.25 \text{ cal.}$

Hence coeff. of emission =
$$\frac{63 \times 1 \times 0.25}{100 \times 50}$$

 $= 0.3003 \text{ calories per second/sq. cm.}]$

12. What is a black body. Why is radiation from a uniformly heated enclosure considered as a black-body radiation.

13. Describe the construction, mode of action and use of a line bolometer when used as an absolute instrument.

14. State Stefan's Law. How can it be experimentally verified.

15. What is Stefan constant. Given methods of measuring it. What is its numerical value.

16. Write an essay on the production of high temperatures in the laboratory.

17. Describe the construction and use of the Disappearing filament Pyrometer. Under what conditions is its use specially recommended.

18. How will you determine the temperature of a flame when it is (i) luminous (ii) non-luminous.

19. Briefly describe what you consider to be the source of solar energy.

CHAPTER XV

THE ATMOSPHERE

Experiment, directed by the disciplined imagination either of an individual or better still, of a group of individuals of varied mental out-look, is able to achieve results which far transcend the imagination alone of the greatest philosopher
—*Lord Rutherford.*

15.1. The atmosphere. We live and move at the bottom of a vast ocean of air of great complexity which is at least 2000 miles in depth. The modern understanding of the atmosphere began with the work of Bort in 1898.

The temperatures, pressure and wind velocities at various altitudes were first determined with the help of sounding balloons fitted with self-recording thermometers, barometers etc. Present-day balloons are fitted with radio devices which continuously send radio-signals to a receiving station, on the ground. The balloons have helped in exploring the atmosphere upto a depth of about 20 miles. The rockets have carried on the exploration upto over 100 miles.

15.2. The atmosphere is now known to consist of three layers or shells surrounding the earth.

1. The Troposphere. It is the region nearest the earth and ranges in height from 10 miles at the equator to 5 miles at the poles. This layer is so closely packed, that although its volume is only $\frac{1}{800}$ th of the total atmosphere, it accounts for 79% of the total weight. On account of a thorough mixing of the air in this region due to vertical convection currents, the proportion of the various gases is very uniform. Dry air contains 78% by weight of nitrogen, 21% of oxygen, 0.9% of argon and 0.03% of carbon-di-oxide, with traces of rare gases, hydrogen and ozone. The percentage of water vapour in the atmosphere is very variable and ranges from 0.005 to 4%. A rising temperature promotes evaporation from water-surfaces and adds to the moisture-content of the atmosphere, while a falling temperature leads to the precipitation of the water vapour. On account of the large latent heat of water, the water-vapour content of the atmosphere is of the utmost importance to the meteorologist in the study of climatic conditions and weather changes.

In this region the temperature falls progressively as height increases, at the rate of about 6°C for each mile of ascent. At a certain height, depending upon the Latitude, the temperature ceases to fall any further. This level is called the **Tropopause** and marks the upper limit of the Troposphere. Lower temperatures *i.e.*, -80°C prevail in the Tropopause above the equator than above the poles where the temperature is -50°C . This is probably due to two reasons :—

(i) As the Tropopause is at a greater height at the equator, the temperature is able to fall considerably at that height.

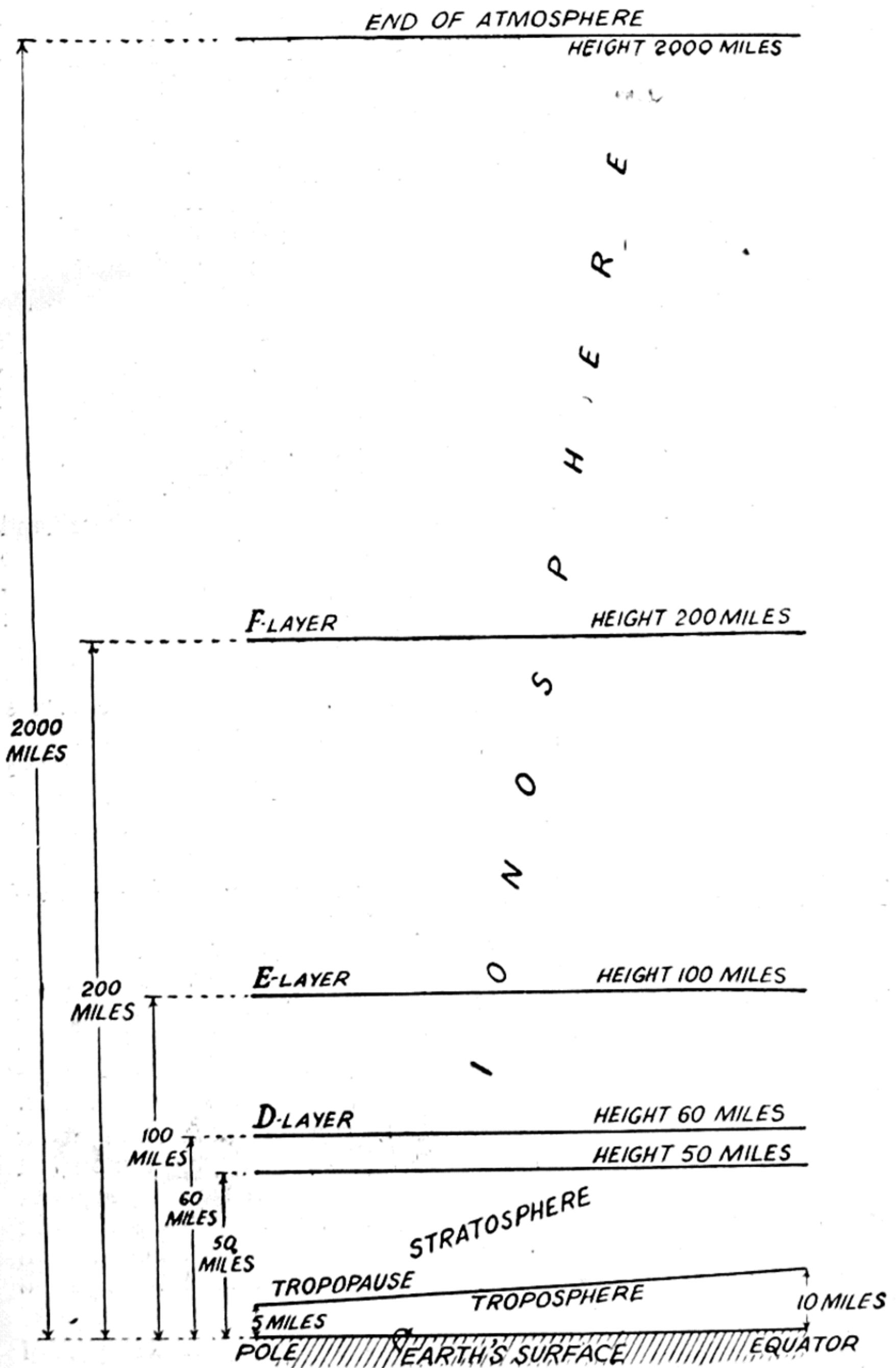


Fig. 15.1. Atmosphere

(ii) Ozone is more abundant at the poles over the Tropopause

and as it is a good absorber of solar radiation, it is quickly heated up by absorbing ultra-violet light.

2. The Stratosphere. It extends above the Tropopause to a height of about 50 miles and occupies 2% of the total volume and 20% of the total weight of the atmosphere. In this region ozone also makes its appearance. Ozone is produced by the dissociation of Oxygen molecules by the ultraviolet radiation from the sun. That is why it is so rare at ground-level but increases in amount with altitude and about 60% of it is concentrated in a region at 20—30 miles. Its layer is thicker and lower at the poles than at the equator. Being a powerful absorber of solar radiation ozone heats the stratosphere to temperatures much higher than those prevailing in the Troposphere.

Lindemann and Dobson have shown that temperature stays constant in the lower stratosphere upto 20 miles. It then continues to rise for about 10 miles. This is probably due to the presence of ozone which is a powerful absorber of ultra-violet radiation. Above this height the temperature begins to fall and drops down below 0°C at the top of the stratosphere *i.e.*, at 50 miles.

3. The Ionosphere. It starts above the stratosphere and extends to over 2,000 miles. It occupies 97% of the total volume but only 0.5% of the total weight of the atmosphere. The gas pressure at 62 miles is 10^{-6} and at 200 miles it is one-ten billionth of that at the surface of the earth. At 100 miles the mean free path between molecules is a few centimeters but at 300 miles it is 125 miles and increases upto 9000 miles or more. The Ionosphere is the earth's frontier with outer space and consists of ionized gas-particles. Over this region fall powerful radiations from the sun, the stars and from interstellar space which produce intense ionization of the gas-molecules. As a result of this ionization, the temperature in the lower Ionosphere rises to over 1500°C in the 300—500 mile zone. Jeans and Spitzer have calculated that the temperature in the upper Ionosphere range from $10,000^{\circ}\text{C}$ to $15,000^{\circ}\text{C}$.

The Stratosphere and the Ionosphere together constitute the upper atmosphere and only the first 500 miles of this are relatively well-known. Information about this is obtained from a study of meteors, comets, Aurora, Solar spectrum, radio-waves and sounds from powerful explosions. Thus by a study of the reflection of radio-waves, the existence of layers of ionized particles has been established.

Very long waves are occasionally reflected at the D-layer, about 60 miles up ; medium waves are reflected at the E-layer beginning at about 100 miles while short waves are reflected at the F-layer about 200 miles up. The reflected waves give important information about the layer which reflects them. The region above 500 miles is yet a sealed book ; it cannot be explored because it affords as yet no clues to the investigator.

There are two possibilities with regard to the uppermost part of the atmosphere :—

(i) Either it passes continuously into a general distribution of matter in thermal equilibrium, filling the surrounding space, or

(ii) It is not in equilibrium and is continually streaming off into space.

One fact will be realized that *space is very thinly populated*. Gamow has calculated that *on the average there is only one atom per cubic metre of space*. The total number of atoms in the Universe is 3×10^{74} .

15.3. Decrease of Pressure with Height. The atmospheric pressure at any level in the atmosphere represents very accurately the total weight of an air column above a unit area situated at the level of the observation plane. If the density of the atmospheric air were the same at all levels, the pressure at sea-level would correspond to a height of about 5 miles only. The density however, decreases rapidly with increasing height. At a height of 7.5 miles the air is only about one-quarter as dense and at 11 miles about one-eighth as dense as at sea level, but even at 80 miles the air is sufficiently dense to resist the movement of meteors and raise them to incandescence. At greater altitudes the pressure is also smaller, because there is a lesser mass of air above the observer. To find the rate of decrease of pressure, consider a vertical air-column of unit cross-section.

At a level y , the pressure is p and at a level $(y+dy)$ it is $(p-dp)$ because as height increases the pressure diminishes. The pressure difference between the two levels, is equal to the weight of an air-column of unit cross-section and dy in height. If dy is small, the density ρ of the air and g , the acceleration due to gravity, may both be considered practically constant between the two levels.

$$\therefore dp = -(1 \times dy) \times \rho \times g$$

$$= -g\rho dy$$

Also if air be dry, $pV = RT$

$$\text{or } p \cdot \frac{M}{\rho} = RT,$$

where M is the molecular weight of the air

$$\therefore \rho = \frac{pM}{RT}$$

Substituting (ii) in (i)

$$dp = -g \cdot \frac{pM}{RT} \cdot dy.$$

$$\text{or } \frac{dp}{p} = -\frac{gM}{RT} dy \quad (iii)$$

Neglecting the variation of g with altitude and integrating (iii)

$$\int \frac{dp}{p} = -\frac{gM}{R} \int \frac{dy}{T}$$

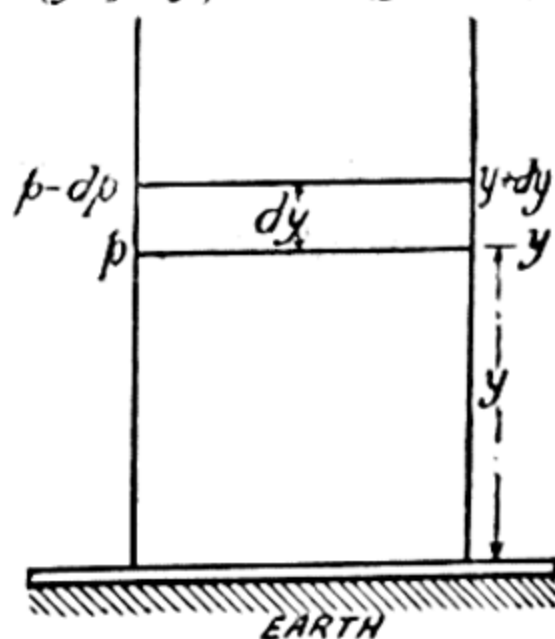


Fig. 15.9.
Variation of Pressure
with height.

$$\text{or } \frac{p}{p_0} = e^{-\frac{gM}{R} \int \frac{dy}{T}}$$

$$\text{or } p = p_0 e^{-\frac{gM}{R} \int \frac{dy}{T}} \quad (iv)$$

where p_0 is the pressure at the earth's surface.

Again, if T is also independent of height, (iv) becomes,

$$p = p_0 e^{-\frac{gM}{RT} y} \quad (v)$$

This is a very important relation. It is due to Halley.

The assumption of a constant temperature in the vertical direction is a good approximation to the average temperature distribution in the upper atmosphere—the *Stratosphere*. In the lower part of the atmosphere called *Troposphere*, the distribution of temperature is better represented by a linear function

$$T = T_0 - \alpha y \quad (vi)$$

α is called the *Lapse Rate* of temperature. Lapse rate is positive if temperature decreases as height increases; it is zero if temperature does not change with altitude; but it becomes negative if temperature increases with height.

If the temperature is a linear function of height, (iv) becomes

$$\begin{aligned} p &= p_0 e^{-\frac{gM}{R} \int \frac{dy}{T_0 - \alpha y}} \\ &= p_0 e^{\frac{gM}{R\alpha} \log \frac{T}{T_0}} \\ &= p_0 \left(\frac{T}{T_0} \right)^{\frac{gM}{R\alpha}} \end{aligned} \quad (vii) \quad [cf. a^x = e^{x \log a}]$$

To correct formula (vii) for the moisture-content of the atmosphere we proceed as follows:—

In our present discussion we are concerned only with the density of air. Since the addition of moisture lowers the density of air, we can substitute for the moist air, dry air at a somewhat higher temperature T' , called *Virtual Temperature*, in our discussion. The virtual temperature

$$T' = \frac{T}{1 - 0.379 \frac{p}{P}}$$

where p is the partial pressure of the water vapour and P the total atmospheric pressure.

15.4. Convective Equilibrium in Atmosphere. As warm air rises up into regions of low pressure, it expands *adiabatically* and cools down. As long as the surrounding region is cooler and therefore denser than this rising current of warm air, the latter continues to rise up and up and the atmosphere is said to be **unstable**. If the adiabatic expansion cools it to a temperature lower than that of the surrounding air, it ceases to rise up any further and in fact, begins to sink down. The atmosphere is now said to be **stable**.

For adiabatic expansion of *dry* air

$$\frac{p^{\gamma-1}}{T^{\gamma}} = \text{constant}$$

or

$$T^{\gamma} p^{1-\gamma} = \text{constant}$$

Differentiating,

$$\gamma \cdot T^{\gamma-1} dT p^{1-\gamma} + T^{\gamma} (1-\gamma) p^{-\gamma} dp = 0$$

or

$$\frac{dT}{dp} = \frac{\gamma-1}{\gamma} \cdot \frac{p^{-\gamma} T^{\gamma}}{T^{\gamma-1} p^{1-\gamma}}$$

$$= \frac{\gamma-1}{\gamma} \cdot \frac{T}{p} \quad \dots \quad \dots \quad \dots \quad (i)$$

The temperature lapse rate

$$\frac{dT}{dy} = \frac{dT}{dp} \cdot \frac{dp}{dy}$$

or

$$\frac{dT}{dy} = \frac{\gamma-1}{\gamma} \cdot \frac{T}{p} \times \frac{dp}{dy} \quad \dots \quad \dots \quad \dots \quad (ii)$$

But from (i) Art. 15.3

$$\frac{dp}{dy} = -g\rho$$

\therefore (ii) becomes

$$\frac{dT}{dy} = -\frac{\gamma-1}{\gamma} \cdot \frac{T}{p} \cdot g\rho \quad (iii)$$

Also from (i. a) Art. 15.3 we have

$$\frac{\rho T}{p} = \frac{M}{R}$$

\therefore

$$\frac{dT}{dy} = -\frac{Mg}{R} \cdot \frac{\gamma-1}{\gamma} \quad (iv)$$

an important relation.

The above calculation though strictly true for dry air holds fairly accurately for moist air also, if its temperature is low, because the absolute amount of water-vapour in air is very little at low temperatures.

If the lapse rate dT/dy for a rising air-current is greater than the lapse rate for the surrounding atmosphere, upward convection stops and atmosphere is stable. If dT/dy is lower, upward movement of air-currents continues and atmosphere is unstable. This instability produces thunderstorms and heavy rainfall. Intense local heating of the earth's surface is an important cause producing instability of the atmosphere.

15.5. Formation of Clouds. Water vapour in the atmosphere results from evaporation from water-surfaces and the amount of water vapour actually present at any place is highly variable and depends upon many factors. On account of the adiabatic expansion due to the upward movement of the water-vapour, the temperature progressively falls with a fall in temperature, the water vapour moves more and more towards saturation and then leads to the precipitation of moisture on the tiny crystals of water-soluble salts which float about in the atmosphere and which act as nuclei in the initial stages of the formation of water drops. Cloud formation is thus solely due to the vertical convection currents in the air, condensation occurring when the dew-point has been reached. This vertical convection may be brought about either by disturbances in the upper layers or by a large-scale surface heating or by the mixing of air-masses at different temperatures etc. The form of the cloud that ultimately forms, depends on the way in which the vertical convection has been brought about. Nearly all the clouds form in the troposphere.

15.6. Bergeron's Theory. Even when the cloud ascends above the level where its temperature is 0°C , condensation to liquid drops continues, *i.e.*, supersaturation occurs and may persist upto levels at as low a temperature as -35°C . How ice formation starts is not yet understood. A few ice-crystals are perhaps present in the cloud below the level where the temperature is -32°C . Above that level their number rapidly increases.

When super-cooled water-droplets and tiny ice crystals exist together in the cloud, the saturation vapour pressure over ice is less than that over the super-cooled water at the same temperature. The resultant vapour pressure adjusts itself to a value in between that of the two saturation pressures. The result is that the environment becomes unsaturated for water but supersaturated for ice, so that water continually evaporates from the drops while the ice crystals rapidly grow in size and then fall through the cloud. By the time they reach the bottom of the cloud they get melted due to friction and form rain-drops.

This process of rain formation was first proposed by Bergeron and is accepted generally as one of the most important ways in which rain may form.

15.7. Artificial rain. We have seen that the formation of rain in a cloud requires the presence of water-droplets and ice crystals. It is thus clear that clouds which are below the freezing level of the atmosphere will not be able to produce rain. But these could be coaxed

to produce rain by seeding them artificially with ice crystals. Langmuir tested the theory by seeding the clouds with granulated dry ice (solid CO_2), at a temperature of 80° below zero. This is intended to induce snow-flake formation among the cloud-droplets to fall either as snow or rain, according to the temperature of the lower air.

Another method involves the use of silver iodide 'smoke' which consists of minute crystals of an atomic structure similar to crystalline ice. Obtained by burning charcoal treated with silver iodide, this expensive smoke is induced into suitable clouds either from aeroplanes or from especially sited furnaces on the ground from which it is claimed to rise high enough to produce a downpour. Both these methods have met with qualified success but definite proof that subsequent rain was due to their employment is impossible to obtain.

Many scientists are of the view that some other conditions should also be fulfilled before a cloud can be induced to produce rain. The conditions are :

(1) The cloud must be some 4000 feet thick and dense enough to contain a large number of droplets.

(2) Wind conditions must be favourable to maintain the right amount of turbulence in the cloud.

(3) Vertical velocities within the cloud must be appreciable.

In other words, *only, those clouds would produce rain after seeding which would shed rain even otherwise. No man can make a cloud and no man can push or pull a cloud to the place where he wants the rain to fall.* Bowen has observed that "it would be quite impossible to do anything for desert areas by this method ; the right type of clouds don't exist there in sufficient quantity. If man wants to bring rain to such an area he must learn to bring clouds and therefore to control the circulation of the atmosphere. This at present is an impossible task. Wendt has observed that if man wants to bring rain to dry areas, it must come from the land or from the sea but not from the sky.

A good deal of time and money is being spent on the scientific problems involved. It is possible that we shall be able to persuade the lower clouds to release their moisture but we shall still not be able to move them about at will or stop their rain when enough has fallen.

Schaefer has observed that seeding may prove more useful in breaking up a storm-cloud than in precipitating it. The latter will enable the air pilots to obtain better visibility during a dense fog, for example.

QUESTIONS

1. Establish a relation connecting the pressure of the atmosphere with height above sea level.

2. Write a brief note on the variation of temperature with altitude.

3. What do you understand by the Convective Equilibrium of the atmosphere.

Establish the relation

$$dT/dy = -\frac{\gamma-1}{\gamma} \cdot \frac{Mg}{R}$$

4. Write an essay on the atmosphere, describing clearly the three belts into which the atmosphere has been divided.

5. Write notes on: (i) Troposphere (ii) Stratosphere (iii) Ionosphere.

6. Why are lower temperatures prevalent in the tropopause over the equator than over the poles.

7. Describe briefly how clouds are formed. Given the Bergeron's theory on the formation of clouds.

8. Write a note on Artificial rain-making.

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